On the evidence that the radiocarbon date of the Turin Shroud was significantly affected by the 1532 fire

John P. JACKSON
Turin Shroud Center of Colorado
et Keith PROPP
Kaman Sciences Corp.

In 1988, the Shroud of Turin, believed by some to be the historic burial cloth of Christ, was subjected to radiocarbon analysis (Ref. 1). Based on direct measurements of the C14/C12 and C13/C12 ratios, it was concluded by a team of twenty-one investigators that the age of the Shroud was medieval, dating from between 1260 - 1390 AD at the 95% confidence level.

In 1996, however, experimental data was published by Kouznetsov et al. from the Sedov Biopolymer Research Laboratories in Moscow, Russia that indicated linen at elevated temperatures can become highly enriched with carbon-14 from the surrounding air (Refs 2,3). Along with time and temperature data showing significant radiocarbon isotopic shifts in linen, it was reported that the radiocarbon age of one incubated sample from the En-Gedi site on the west shore of the Dead Sea in Israel changed from about 2175 BP (Before Present) to 800 BP following a one hour incubation at a modest 200 C.

These data, however, were immediately challenged by Jull et al. who were part of the University of Arizona team that radiocarbon dated the Shroud in 1988 (Ref 4,5). They reported results of an experiment to test the results of Kouznetsov et al. but failed to detect any significant isotopic shifts of carbon-13 or 14 relative to carbon-12 in their incubated linen sample, which also came from the En-Gedi site. In addition, theoretical evaluations of the Russian experiment have led the French mathematician Salet to find certain theoretical inconsistencies with Kouznetsov's interpretation of his experiment (Ref 6).

In view of such objections to the Russian experiment, we decided to perform our own theoretical evaluations of the reported data, which are detailed in the present paper. It is our conclusion that the Kouznetsov et al. heating experiments are internally consistent within the context of an attachment/exchange model that we have developed. Moreover, we show that this model can satisfy the objections raised by Jull et al. and Salet. Finally, we show that multi-century shifts in the radiocarbon age of the Shroud of Turin are indeed plausible from reasonable assumptions concerning the 1532 fire in which parts of the Shroud were clearly heated to the point of scorching. When considering isotopic effects associated with the fire via the Russian experiments, we think that the possibility the Shroud dates to the First Century cannot be excluded by the 1988 radiocarbon measurement. Moreover, we conclude that, unless the Kouznetsov et al. data can be invalidated by a properly executed experiment, any future attempt to re-radiocarbon date the Shroud would be meaningless due to the large uncertainties associated with the 1532 Chambrey fire and probable extent of the isotopic contamination resulting from that fire.

Theoretical Considerations

Let us begin by considering the experimental time data for an incubation of the En-Gedi sample at 200 C by Kouznetsov et al. (Ref 2 - Figure 7), and replotted for convenience below in Figure 1.

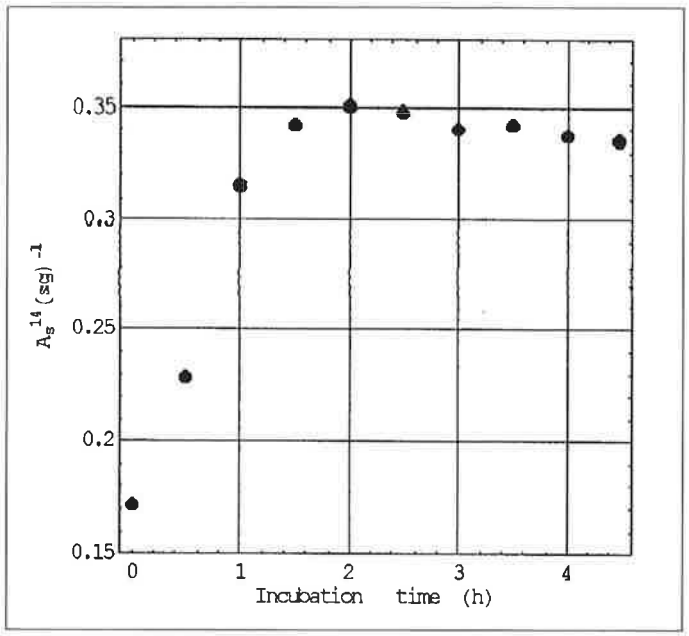


Figure 1.
C-14 Activity (dps g^{-1}) versus time at 200 C
1996 Russian Data (Ref 2)

This data shows that the specific radiocarbon activity, As^{14}, of the heated linen sample increases dramatically from approximately 0.17 to 0.35 disintegrations per second per gram (dps g^{-1}) of sample carbon in about two hours[1]. Following this rise, we then see a slow decrease in As^{14} over the next two and one half hours of the four and one half-hour experiment. In Kouznetsov's Figure 8 (Ref 2), and replotted below in Figure 2, we see a similar behavior in the C-13 deviation, δs^{13}, of the sample.

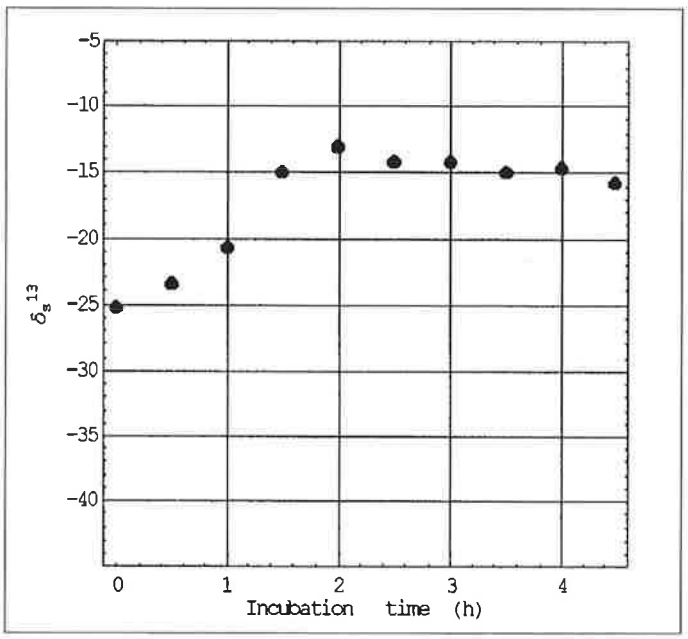


Figure 2.
C-13 deviation versus time;
1996 Russian Data at 200 C (Ref 2)

Because the curves of Figures 1 and 2 appear to be reasonably well behaved, it seems reasonable to expect that they could be described by a simple transfer model that respects simultaneous conservation of the carbon-12, 13, and 14 isotopes.

Insight into developing an appropriate model can be obtained by first considering some earlier data published by Kouznetsov et al. in 1993 (Ref 7). In particular, Figure 2 of that data, replotted below as Figure 3, shows that the ratios of C-13 and C-14 to C-12 in air decrease at the same time those of the heated linen sample increase.

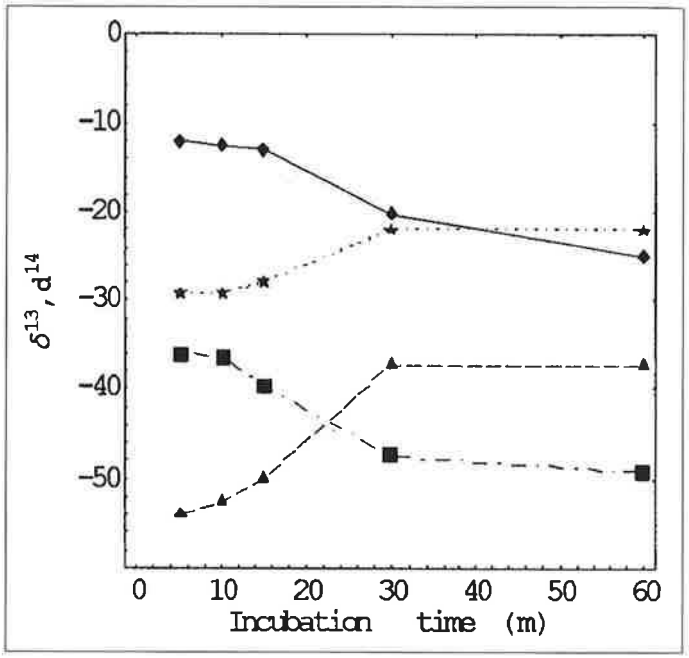


Figure 3.
1993 Rome Data at 140 C (Ref 7)
Top to Bottom at Left
(C-13 air, C-13 linen, C-14 air, C-14 linen)

After about 30 minutes of exposure at 140 C, the time variations in both the C-13 and 14 ratios for air and linen simultaneously and markedly cease for the remaining 30 minutes of the one hour incubation experiment.

It is thus clear that the apparent isotopic enrichment of the linen sample involves one or more mechanisms that affect the isotopic characteristics of the surrounding air as well. There are three basic ways this could occur: (1) Transfer of carbon isotopes from the air to the linen, (2) Transfer from the linen to the air, and (3) exchange of carbon isotopes between the air and linen. The problem is to decide which transfer type (or combinations thereof) could explain the Russian data.

In both the Figures 1 and 2 data, we observe an initial rise followed by a slow decrease in the C-13 and 14 ratios (relative to C-12) of the sample. The latter effect is not observed in the Figure 3 data, possibly because this data was recorded at a lower temperature (140 C) than for the Figure 1 and 2 data (200 C)[2]. This suggests that two transfer mechanisms are in general needed to explain the Russian data.

We expect that the air to linen transfer and the exchange Modes (#s 1 & 3 above) would favor the heavier isotope while the linen to air Mode (#2) would favor the lighter isotope. Accordingly we suppose that Mode #2 is inconsistent with both the rising part of the A_s^{14} curve in Figure 1 (since this would imply a substantial loss of the most abundant C-12 isotope from the sample) and the decreasing portion (since Mode #2 would be expected to increase the C-13/C-12 and C-14/C-12 ratios in the linen). Likewise the air to linen Mode (#1) would not account for the late time isotopic decrease shown in Figures (1 & 2), but the exchange Mode (#3) could. Under certain assumptions[3], the exchange Mode (#3) could account for the rise in isotopic enrichment, but then we are left without a different mode by which to account for the decrease (since we have eliminated Modes #1 and 2 for the decreasing portion). Thus, by process of elimination, we are led to propose that the Russian data might be explained by a combination of Modes #1 and 3, with the former accounting for the rising portion of the data and the latter for the decreasing part.

Such an implied transfer of carbon between air and linen must logically occur via some chemical structures that contain carbon. In the Russian experiments the only carboncontaining compounds in the air were carbon monoxide and carbon dioxide. However, based on the concentrations of air carbon quoted in the Russian experiments (Refs 2,3), the degree of reported radiocarbon enrichment (~ 1 x 10^7 C-14 atoms per mg of sample) could only have come from C-14 associated with carbon dioxide (~ 4 x 10^7 C-14 atoms in their experimental chamber of 5 000 cm^3), as the amount contained in carbon monoxide is trivial (~ one C-14 atom in the 5000 cm3 chamber)[4].

Kouznetsov et al. have looked for chemical changes that occurred in the linen sample as a result of the heating process. Using infrared and mass-spectral analysis of the incubated samples, they report observing significant addition of carboxyl groups on approximately 20% of the cellulose molecules (Refs 2,3). As these carboxyl groups contain carbon that was not originally part of the cellulose (before incubation), it is logical to consider that these carboxyl groups may be by-products of transfer Mode #1 from the air carbon dioxide in some fashion.

In summary, then, we propose the following hypothesis to explain the Kouznetsov et al. data. At elevated temperatures, certain interaction pathways are activated that allow carbon dioxide to interact with the linen cellulose so as to form attached carboxyl groups[5]. We propose that the formation of such attached carboxyl groups occurs via a highly, albeit slow, non-equilibrium process (in the isotopic sense). The rise of C-13 and to greater extent C-14 concentrations relative to C-12 in the carboxyl contamination is because the transfer rate constant for the carboxylation process involved is isotopically dependent. In time, however, the initial disequilibrium in isotopic concentrations of the attached carbon are returned to statistical equilibrium by an exchange pathway also operative at the elevated temperature between the air carbon dioxide and attached carboxyl groups5. If the cellulose sample is removed from the thermal environment before the exchange process can achieve isotopic equilibrium with the air, the carboxyl contamination will contain the statistical imprint of the non-equilibrium isotopic distribution at the time of its removal and therefore affect the overall radiocarbon age of the contaminated sample.

In the remainder of this paper, we present a theoretical model that incorporates these essential ideas. Using this model, we shall show that it mathematically predicts the Russian data and simultaneously accounts for the nullity of the Arizona experiment (Refs 4,5). We also discuss how this mechanism could have affected the 1988 radiocarbon date of the Shroud. Our analysis differs from the critiques of Jull et al. (Refs 4,5) and Salet (Ref 6) in that our model does not assume that the isotopic ratios of the carboxyl contamination are the same as that in the air from which it came[6,7].

Development of Model

Let us now consider a linen sample of mass **M** that has been incubated in a carbon dioxide containing atmosphere of volume **V**. To explain the Russian data, we hypothesize that carboxyl groups form on the sample from the air carbon dioxide, thereby incorporating onto the sample extraneous carbon from the environment (by some molecular process). Thus, we may express the total carbon content of the contaminated sample as

$$N_t^m = N^m + N_l^m \qquad (1)$$

where

N_t^m = total number of carbon atoms of isotopic type **m** in the sample (including the contamination)

N^m = number of carbon atoms of isotopic type **m** in the carboxyl contamination only

N_l^m = number of carbon atoms of isotopic type **m** in the base cellulose (of the linen sample)

m = 12,13,14

In terms of the standard formalism as originally proposed by Stuiver and Pollach (Ref 8) and used in the Russian experiments as well as in the 1988 Radiocarbon dating of the Shroud, the fractional deviations from the laboratory standard for C-13 and C-14 are defined for any amount of carbon isotope of type m, n^m, as follows[8,9]:

$$\delta^{13} = \left(\frac{\left(\frac{n^{13}}{n^{12}}\right)}{\left(\frac{n^{13}}{n^{12}}\right)_{ref}} - 1 \right) 1000 \qquad (2)$$

$$d^{14} = \left(\frac{\left(\frac{n^{14}}{n^{12}}\right)}{\left(\frac{n^{14}}{n^{12}}\right)_{ref}} - 1 \right) 1000 \qquad (3)$$

Using Equation (1), we can express the isotopic deviations for the sample (δ_s^{13}, d_s^{14}) in terms separate deviations for the base linen (δ_l^{13}, d_l^{14}) and carboxyl contamination (δ^{13}, d^{14}) by[10]

$$\delta_s^{13} = \beta (\lambda \delta^{13} + \delta_l^{13}) \qquad (4)$$

$$d_s^{14} = \beta (\lambda d^{14} + d_l^{14}) \qquad (5)$$

where

$$\lambda = \frac{N^{12}}{N_l^{12}} \qquad (6)$$

$$\beta = \frac{1}{\lambda + 1} \qquad (7)$$

During the incubation, only the terms associated with the carboxyl contamination, δ^{13}, d^{14}, β, and λ, are affected. The deviations for the base linen δ_l^{13} and d_l^{14} remain constant. Thus, to calculate the overall isotopic changes in the sample, we need only track the isotopic content of the carboxyl carbon added to the cellulose.

For reasons stated above, we consider that the isotopic changes occurring in the sample during heating are due to an interaction between the gaseous carbon dioxide and the fibril which produces chemically bound carboxyl contamination onto the cellulose. This interaction, however, will not only be confined to the external surfaces of the fibrils, but within the interior bulk of the fibrils as well due to gaseous diffusion into the fibrils by the carbon dioxide.

Such gaseous penetration of carbon dioxide can be inferred by noting that gaseous water vapor is well known to penetrate into a fibril by diffusion (Ref 9). The diffusion coefficient for this process is approximately 1 x 10^{-7} cm^2/s. For a typical fibril of radius 1 x 10^{-3} cm, the diffusion time for complete vapor penetration of the fibril is

$$\tau = \frac{(10^{-3})^2}{2 \times (1 \times 10^{-7})} = 5s$$

Since carbon dioxide molecules are only about 69% larger than water molecules (Ref 10), we can expect penetration of CO_2 into the linen fibrils on a similar time scale.

Because this time is short by orders of magnitude than the time scale of the Russian Experiment ((~ 5000 s), see Figures 1 & 2), the linen fibrils have sufficient time to become uniformly dispersed throughout their bulk with gaseous carbon dioxide, thereby allowing the carboxyl reactions with the cellulose to occur within. Indeed, Kouznetsov et al. report that 20% of the cellulose molecules are carboxylated, a result that could not occur unless carbon dioxide had indeed penetrated into the interior mass of the linen fibrils (Refs 2,3). That the carboxylation is not complete is likely due to the lack of gaseous diffusion into the closely packed (crystalline) molecular regions (~ 0.01 microns in size) within the fibril as well as into some intermolecular cross-linking regions that make some hydroxyl groups unavailable to accommodate a carboxyl group.[11, 12]

We now propose that the isotopic content of the carboxyl groups formed on the cellulose from the air (via the Modes #1 and 3 transfer processes discussed above) can be expressed in terms of the following rate equations:

$$\frac{dn^{12}}{dt} = k^{12} n_a^{12} (n - n^{12} - n^{13} - n^{14}) + k_{23} n_a^{12} n^{13} + k_{24} n_a^{12} n^{14} - k_{32} n_a^{13} n^{12} - k_{42} n_a^{14} n^{12} \qquad (9)$$

$$\frac{dn^{13}}{dt} = k^{13} n_a^{13} (n - n^{12} - n^{13} - n^{14}) + k_{32} n_a^{13} n^{12} + k_{34} n_a^{13} n^{14} - k_{23} n_a^{12} n^{13} - k_{43} n_a^{14} n^{13} \qquad (10)$$

$$\frac{dn^{14}}{dt} = k^{14} n_a^{14} (n - n^{12} - n^{13} - n^{14}) + k_{42} n_a^{14} n^{12} + k_{43} n_a^{14} n^{13} - k_{24} n_a^{12} n^{14} - k_{34} n_a^{13} n^{14} \qquad (11)$$

$$\frac{dn_a^m}{dt} = -\frac{dn^m}{dt} \qquad (12)$$

where

n^m = solid state concentration of carbon atoms of isotopic type m (i.e. 12, 13, 14) associated with the attached carboxyl groups within the sample (cm^{-3})

n_a^m = gaseous concentration of carbon atoms of isotopic type m in the air carbon dioxide within the sample (cm^{-3})

k^m = rate constant for producing from the air a carboxyl group within the sample containing a carbon of isotopic type m ($cm^3 s^{-1}$) [13]

k_{jk} = rate constant for replacement of a carbon isotope (**1 k**) within the carboxyl contamination by isotope (1 j) from the air carbon dioxide where **j, k**= 2,3,4 ($cm^3 s^{-1}$) [14]

n = concentration of possible attachment sites for carboxylation in the sample (cm^{-3})

Equations (9-11) state that the rate of accumulation of isotopic type m carbon on the sample can in general be changed by (1) the direct addition of carboxyl groups onto the cellulose (first term of each equation) and (2) exchange (last four terms of each equation). For example, the first exchange term in Equation (9), $k_{23}\, n_a^{12}\, n^{13}$, gives the rate by which C-12 replaces C-13 (via some molecular process) in the existing contamination. Since this involves increasing the number of C-12 atoms, this rate is counted as positive in the C-12 rate equation. This same rate also appears in the third exchange term shown in Equation (10), but as a negative contribution since the exchange decreases the amount of C-13 in the contamination for the C-13 rate equation. In this way, the exchange terms do not change the total number of carboxyls, only the relative number of the various isotopes contained within the carboxyl contamination [15]. Equation Set (12) is an expression of conservation for the three isotopic varieties in transferring from air to linen.

The system of coupled Equations (9-12) can be simplified if we assume that the isotopic concentration is uniform throughout the chamber (including within the fibrils), implying that we can replace the atmospheric concentrations, $n_a{}^m$, by (N_a^m / V) where N_a^m is the total number of C-m (where m = 12, 13, 14) isotopes in the air and **V** the volume of the chamber. This assumption is justified by considering the diffusivity for air given by (Ref 10)

$$D = \frac{2}{3}\left(\frac{1}{\sigma P}\right)\left(\frac{k^3 T^3}{\pi \mu}\right)^{1/2} \qquad (13)$$

which, at atmospheric pressure **P** and temperature **T** = 200 C, is about 0.15 cm^2/s for CO_2 with molecular cross-section σ and mass μ [16]. The volume, **V**, of the incubation chamber in the Russian Experiment was 5000 cm^3 (see below) for which the cubic linear dimension is about 17 cm. Thus, the time for diffusion effects to move across the chamber is about $(1/2)(17cm)^2 / (0.15\ cm^2/s) \sim 1000$ seconds, somewhat less than the 5000 second time scale of the experiment (See Figures 1 & 2) [17].

Because the diffusion times within the individual fibrils are even shorter (~ 5 s) than the chamber diffusion time (~ 1000 s) which is less than the characteristic time of the experiment (~ 5000 s), we may assume that the CO_2 concentration within the fibrils is equal to that uniformly distributed across the entire chamber volume of the Russian experiment. Thus we can express Equations (9-12) for the transfer processes occurring within the fibrils as [18]

$$\frac{dN^{12}}{dt} = K^{12} N_a^{12} (N - N^{12} - N^{13} - N^{14}) + K_{23} N_a^{12} N^{13} + K_{24} N_a^{12} N^{14} - K_{32} N_a^{13} N^{12} - K_{42} N_a^{14} N^{12} \qquad (14)$$

$$\frac{dN^{13}}{dt} = K^{13} N_a^{13} (N - N^{12} - N^{13} - N^{14}) + K_{32} N_a^{13} N^{12} + K_{34} N_a^{13} N^{14} - K_{23} N_a^{12} N^{13} - K_{43} N_a^{14} N^{13} \qquad (15)$$

$$\frac{dN^{14}}{dt} = K^{14} N_a^{14} (N - N^{12} - N^{13} - N^{14}) + K_{42} N_a^{14} N^{12} + K_{43} N_a^{14} N^{13} - K_{24} N_a^{12} N^{14} - K_{34} N_a^{13} N^{14} \qquad (16)$$

$$\frac{dN_a^m}{dt} = -\frac{dN^m}{dt} \qquad (17)$$

where

$$K^m = \frac{K^m}{V}, \qquad K_{jK} = \frac{K_{jK}}{V} \qquad (18)$$

and

$N_a{}^m$ = total number of carbon atoms of isotopic type **m** (i.e. 12, 13, 14) in the air carbon dioxide within the volume **V**

N^m = total number of possible carbon atoms of isotopic type **m** in the attached carboxyl groups

N = number of attachment sites for carboxylation in the sample available to the transfer process

Along with this equation set, we impose the initial condition of zero carboxylation [19] and initial amount of isotopic carbon dioxide in the chamber,

$$N^m(0) = 0, \qquad N_a^m(0) = N_{a0}^m \qquad (19)$$

where

N_{a0}^m = initial number of air carbon atoms of isotopic type **m** in chamber of Volume **V**.

It is possible to obtain an approximate analytic solution to Equations (14-19) if we make the following simplifying assumptions:

$$N^{14} \leq\leq N^{12}, N^{13}$$

$$N^{m} \leq\leq N_a^{m} = N_{a0}^{m} \qquad (20)$$

$$K_{ij} = K$$

The first inequality expresses the fact that the relative abundance of the C-14 isotope is expected to be orders of magnitude smaller than either C-12 (by 1×10^{-12}) and C-13 (by 1×10^{-10}). The second inequality assumes that the chamber volume contains sufficient amount of each isotope that the total quantity of that isotope in the air does not change appreciably during the carboxylation process. And, finally, we ignore for mathematical tractability any isotopic variability of the exchange rate constant.[20]

Under these approximations, Equations (14-16) subject to the initial conditions of Equation (19) yield the following analytic solution[21];

$$N^{12} = \hat{N}\,[(1 - \alpha)(1 - e^{-bt}) + \alpha(1 - \hat{\beta})(1 - e^{-\hat{b}t})] \qquad (24)$$

$$N13 = \hat{N}\,[(\hat{\gamma} - \alpha\gamma)(1 - e^{-bt}) + \alpha(1 - \hat{\beta})(1 - e^{-\hat{b}t})] \qquad (25)$$

$$N^{14} = \left(\frac{U}{B}\right)(1 - e^{-\hat{b}t}) + \left(\frac{W}{b - \hat{b}}\right)(e^{-bt} - e^{-\hat{b}t})] \qquad (26)$$

where

$$\hat{N} = \frac{N}{(1 + \hat{\gamma})(1 - \alpha\hat{\beta})}$$

$$\gamma = \left(\frac{K^{13}}{K^{12}}\right)\left(\frac{n_{a0}^{13}}{n_{ao}^{12}}\right)$$

$$\hat{\gamma} = \frac{n_{a0}^{13}}{n_{ao}^{12}}$$

$$b = K^{12}\, n_{a0}^{12}\,(1 + \gamma)$$

$$\hat{b} = K\; n_{a0}^{12}\,(1 + \hat{\gamma}) \qquad (27)$$

$$\alpha = \frac{K^{12}}{K}$$

$$\hat{\beta} = \frac{1 + \gamma}{1 + \hat{\gamma}}$$

$$U = N n_{a0}^{14} K$$

$$W = - N n_{a0}^{14} (K^{14} - K)$$

As can be seen from Equation Set (27), the solution is uniquely defined if we know the following parameters:

A. Number of initial isotopic carbon dioxide molecules: $\mathbf{n_{a0}^{m}}$

B. Number of possible carboxyl attachment sites in the sample: **N**

C. Rate constants: $\mathbf{K^{m}}$, **K**

Let us now consider what experimental information is required to determine these fundamental parameters in order to arrive at a unique solution. The parameters contained in Sets (A and B) can be calculated from the following series of Equations (28-30) that connect to experimental parameters:

where

$$n_{a0}^{13} = (f_{1312})\, n_{C02}$$
$$n_{a0}^{14} = (f_{1412})\, n_{C02} \qquad (28)$$
$$n_{a0}^{12} = n_{C02} - n_{a0}^{13} - n_{a0}^{14}$$

$$f_{1312} = \left(\frac{\delta_a^{13}}{1000}\right) + 1 \quad \left(\frac{n^{13}}{n^{12}}\right)_{std}$$

$$f_{1412} = \left(\frac{d_a^{14}}{1000}\right) + 1 \quad \left(\frac{n^{14}}{n^{12}}\right)_{std}$$

$$n_{C02} = \frac{P_{C02}\, V}{kT_0} \qquad (29)$$

and

$\mathbf{P_{C02}}$ = partial pressure $C0_2$

V = volume of chamber (5000 cm^3)

To = temperature when chamber was sealed (~ 20 C)

k = Boltzmann Constant

δ_a^{13}, d_a^{14} = initial air deviations for C-13 and C-14 relative to C-12

The number of attachment sites, **N**, is related to the total number of carbon atoms in the linen, $\mathbf{n_{linen}}$, in the sample by[22]

$$N = f_N n_{linem} \qquad (30)$$

where

$$f_N = \left(\frac{P_C}{100}\right) \quad \left(\frac{1}{6}\right)$$

P_C = % cellulose monomers carboxy lated once (on the average)

$$\text{nlinen} = \frac{0.44 M N_{AV}}{M_{avg}}$$

M = mass of sample (assumed dehydrated and 100% cellulose)

$$Mavg = \frac{12 + 13g_{1312} + 14g_{1412}}{1 + g_{1312} + g_{1412}}$$

$$g_{1312} = \left(\frac{\delta_i{}^{13}}{1000}\right) + 1\left(\frac{n^{13}}{n^{12}}\right)_{std}$$

$$g1412 = \left(\frac{d_i{}^{14}}{1000}\right) + 1\left(\frac{n^{14}}{n^{12}}\right)_{std}$$

N_{AV} = Avagadro's Number

Thus, for problem set specification in Parts A and B above, we need to know (as per Equations (28-30) nine experimental parameters: $\mathbf{P_{CO2}}$, **V**, $\mathbf{T_0}$, $\boldsymbol{\delta_a{}^{13}}$, $\mathbf{d_a{}^{14}}$, $\mathbf{P_C}$, **M**, $\boldsymbol{\delta 1^{13}}$, **and** $\mathbf{d_i{}^{14}}$. It turns out, however, that we can only find three unambiguously reported in the Russian 1996 paper (Ref 2,3), namely $\mathbf{P_{CO2}}$ **= 0.03% atmosphere,** $\boldsymbol{\delta_i{}^{13}}$ **= -25.3**, and $\mathbf{d_i{}^{14}}$ **= -237.8** [23]. The remainder of the empirical parameters requires varying degrees of assumptions.

The authors report measuring a value for $\mathbf{P_C}$ **of 20%**; however, this apparently comes from a textile material different from the En-Gedi textile that was used in the Figure 1 and 2 data shown in this paper (Refs 2,3). It is therefore not clear that this value applies to the En-Gedi sample and, even if it does, whether or not this sample may have been pre-carboxylated to some extent (i.e. partially saturated) before the Russian heating experiments were applied to it. Nevertheless, we shall use this value for **Pc** .

The volume of the chamber is not provided in the paper, but based on our own knowledge of Kouznetsov's laboratory [24] and from information provided by an overseer of these experiments (Ref 13), we understand the chamber volume **V to have been 5000 cm³**.

The isotopic deviations for air, while not very critical, were estimated by referring to the starting values of the Russian 1993 heating experiments as seen in Figure 3 above, assuming that the isotopic characteristics of the air used in the 1996 data were similar. Thus, we assume that $\boldsymbol{\delta_a{}^{13}}$ **= -12.0** and $\mathbf{d_a{}^{14}}$ **= -36.5**.

Finally, we relied on the following information and logic to derive a tentative mass for the samples used in Kouznetsov's 1996 experiment [25]. We have learned that Kouznetsov received 25 mg of a 50 mg En-Gedi sample acquired from the Israel Antiquities Authority by Moroni (Ref 14). In Figures 7 and 8 (Ref 2) we note that isotopic deviations were reported for 17 distinct times and temperatures. Because these data points were determined by the AMS method (Refs 2,3), which necessarily destroys the sample, we estimate the sample mass (for each data point) to be no greater than 1.5 mg (dividing 25 mg by 17.) Accordingly, we have chosen for this paper a nominal value for **M of 1.0 mg** (dehydrated cellulose), [26] recognizing that the equations and methodology outlined in this paper could be applied to any mass which, of course, would alter our results accordingly.

As explained above, we also need the four rate constants of Part C in order to arrive at a well-defined solution of the analytic Equation Set (24-27). One possible method of determining the rate constants appropriate for the Russian data, assuming that our equations in fact model that data, would be to compare various solutions (consistent with the data specifications of Parts A & B) for arbitrary sets of rate constants arrived at by trial and error. However, this procedure is time consuming and computationally inefficient. Moreover, it would not be clear that we have found a satisfactory combination of rate constants for a given fit to the experimental data.

On the other hand, we are in possession of an approximate analytic solution from which we could derive four mathematical conditions that would allow us to compute the four rate constants that we seek, thereby defining all parameters necessary to arrive at a solution. [27]. For this, we used the following four independent conditions that we estimated from the data of Figures 1 and 2:

1. The maximum value of the $\mathbf{A_s{}^{14}}$ activity curve (Figure 1)
2. The time at which the maximum in the $\mathbf{A_s{}^{14}}$ activity curve occurs (Figure 1)
3 . The late time slope of the $\mathbf{A_s{}^{14}}$ activity curve (Figure 1)
4. The maximum value of the $\boldsymbol{\delta_s{}^{13}}$ curve (Figure 2)

Using the analytic solution, we derived four equations containing the four rate constants for each of the above conditions. We then solved the set of equations to give expressions for each of the rate constants. This procedure is quite complex but straightforward and so we only give here the values that we calculated [28].

$\mathbf{K^{12}}$ =	**3.7 x 10^{-24} s^{-1}**	**(attachment, C-12)**
$\mathbf{K^{13}}$ =	**6.2 x 10^{-24} s^{-1}**	**(attachment, C-13)**
$\mathbf{K^{14}}$ =	**2.6 x 10^{-22} s^{-1}**	**(exchange)**
K=	**1.4 x 10^{-24} s^{-1}**	**(exchange)**

In terms of the standard rate constants via Equation (18) corrected for volume (5000 cm^3), we have

k^{12} = 1.9×10^{-20} cm^3 s^{-1} (attachment, C-12)

k^{13} = 3.1×10^{-20} cm^3 s^{-1} (attachment, C-13)

k^{14} = 1.3×10^{-18} cm^3 s^{-1} (attachment, C-14)

k= 7.0×10^{-21} cm^3 s^{-1} (exchange)

Next, we inserted all the parameters, as determined above, into a special computer program [29] that solves Equations (14-19) numerically. Using the functions $N^m(t)$ so derived, we then calculated $\delta_s^{13}(t)$ for the sample using Equation (4). We determined the sample activity $A_s^{14}(t)$ according to the relation,

$$A_s^{14} = \frac{(N_I^{14} + N^{14})\,\lambda^{14}\,N_{AV}}{12\,(N_I^{12} + N_{12}) + 13\,(N_I^{13} + N^{13}) + 14\,(N_I^{14} + N^{14})} \quad (31)$$

where

$$\frac{1}{\lambda^{14}} = \frac{(-5730 \text{ years})}{\ln(1/2)}$$

Our solutions, superimposed on the Russian data are shown in Figures (4 & 5). It is evident that, considering the uncertainties of the input parameters, the solutions are in substantial quantitative agreement with the data.

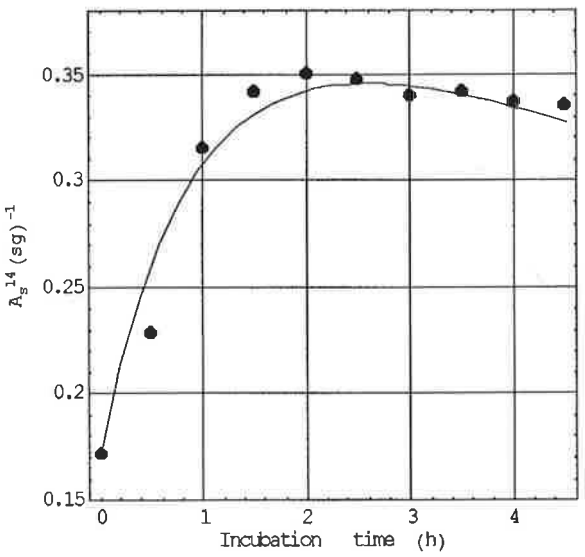


Figure 4
A_s^{14} (dps g^{-1}) Numerical Solution compared to 1996 Russian data at 200 C

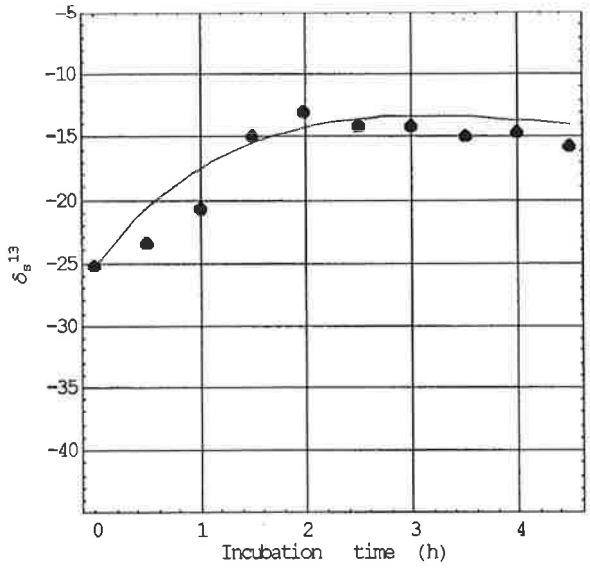
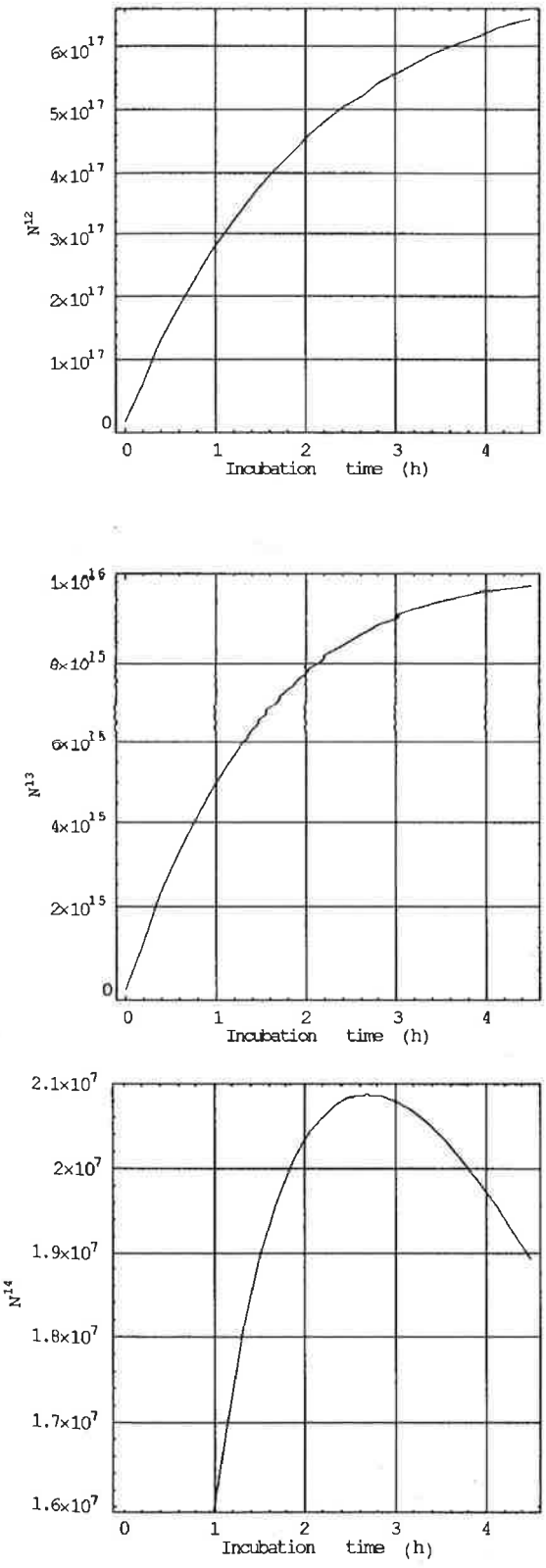


Figure 5.
δ_s^{13} Numerical Solution compared to 1996 Russian data at 200 C

In order to assess the significance of these solution fits to the experimental data, let us recall that our solutions are the result of numerical integrations of the six coupled differential rate Equations (14-17), subject to the initial conditions expressed by Equations (19). We have shown above that the solutions **$N^m(t)$ (m=12, 13, 14)**, used to construct **$\delta_s^{13}(t)$ and A_s^{14} (t)**, are defined by eight parameters: **n_{a0}^m, N, K^m, and K**. In an a-priori sense, we do not know the four rate constants **K^m and K** and so these have been determined using four of eight defining graphical characteristics of the Russian data. [30] The remaining four variables, **n_{a0}^m** and **N (m=12, 13, 14)**, can be determined from nine empirical parameters: **P_{C02}, V, T_0, δ_a^{13}, d_a^{14}, P_C, M, δ_I^{13}**, and **d_I^{14}**. However, we can consider, for all practical purposes, that only three of these nine variables are important, resulting in a dependency of $\delta_s^{13}(t)$ and A_s^{14} (t) on the ratio **(M/V)** and **P_C**. [31] Therefore, unless we use appropriate values for (M/V) and the variable **P_C**, the resulting numerical solution will not reproduce simultaneously all eight graphical characteristics exhibited by the $\delta_s^{13}(t)$ and A_s^{14} (t) data. This is shown explicitly in the Appendix where we provide actual computer solutions for cases where the above parameters were varied somewhat from the baseline values that give the solutions plotted in Figures 4 and 5. Therefore, from these perspectives, we think it is significant that our numerical solutions closely match the published Russian data using reasonable values for **M, V**, and **P_C** that were associated (non-graphically) with this experiment.

The diagrams of Figure 6 below show the calculated isotopic contents of the contamination and air for the Russian 1996 data as a function of time. Notice that saturation was not quite reached at the end of the experiment (~ 4 hrs) because the major isotopic component of the

contamination, N^{12}, is still increasing (slightly). We note that the C-14 content of the air was changed significantly during the incubation. We also see that the effects of both the attachment (positive slope) and exchange processes (negative slope) are evident in the contamination C-14 plot.



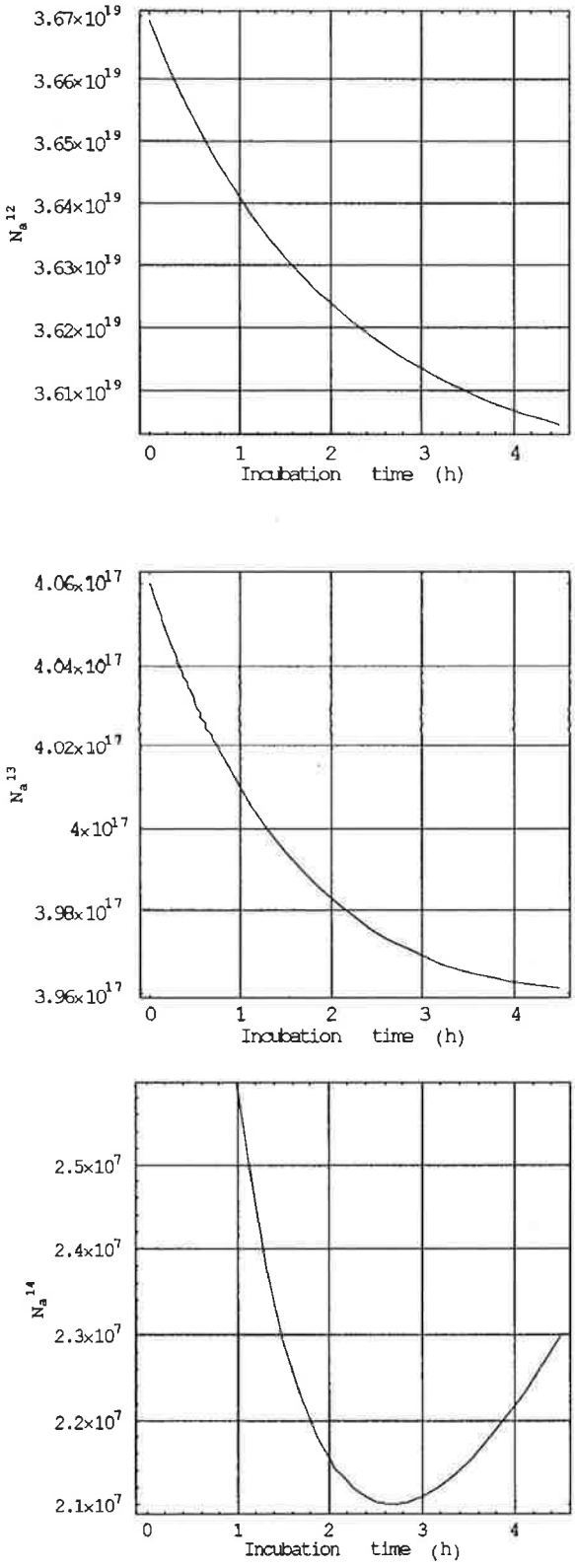


Figure 6.
Isotopic content of the carboyl contamination (left) and air (right) for C-12, 13, and 14 (top to bottom respectively) calculated for the Russian 1996 data at 200 C

Figure 7 shows normalized versions of these data in air.

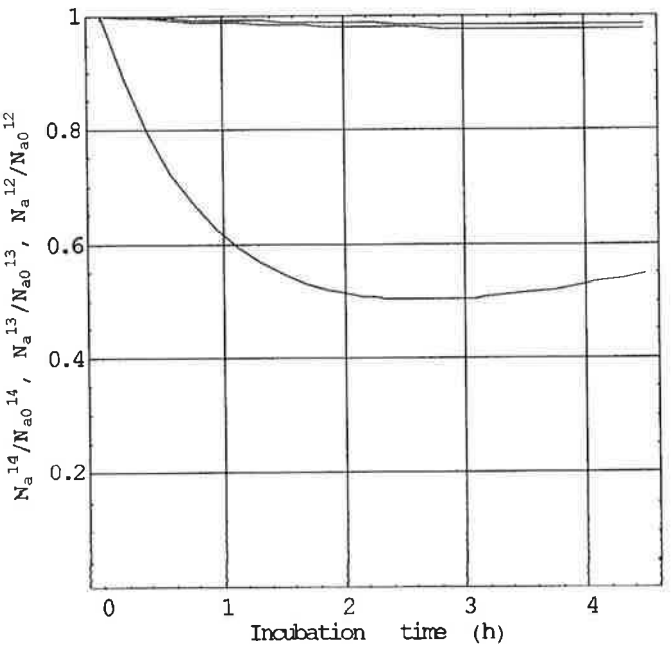


Figure 7.
Calculated Isotopic concentrations in air normalized to initial levels at 200 C
Curves in descending order from the top are: C-12, C-13, C-14.

It is of interest to use our model, which we can now regard as being calibrated to the isotopic enrichment process observed by Kouznetsov et al. at 200 C, to calculate the expected time characteristics of the University of Arizona experiment noted at the beginning of this paper (Refs 4,5). Since this experiment was also performed at 200 C, the rate constants determined above (when properly corrected for volume) should apply [32].

The conditions of the Arizona experiment were different from the Russian experiment [33]. We computed the parameters used in our calculations to model the Arizona experiment (as performed) from information provided (Refs 4,5).

These were as follows [34, 35, 36] :

P_{CO2} = 0.06 atmospheres,
V = 50.0 cm³,
T = 200 C,
δ_a^{13} = - 17.8,
d_a^{14} = + 369.7,
P_C = 20%,
M = 3.6 mg,
δ_I^{13} = - 25.3,
d_I^{14} = - 239.6

Figure (8) shows the calculated results for δ_s^{13} and A_s^{14}. [37]

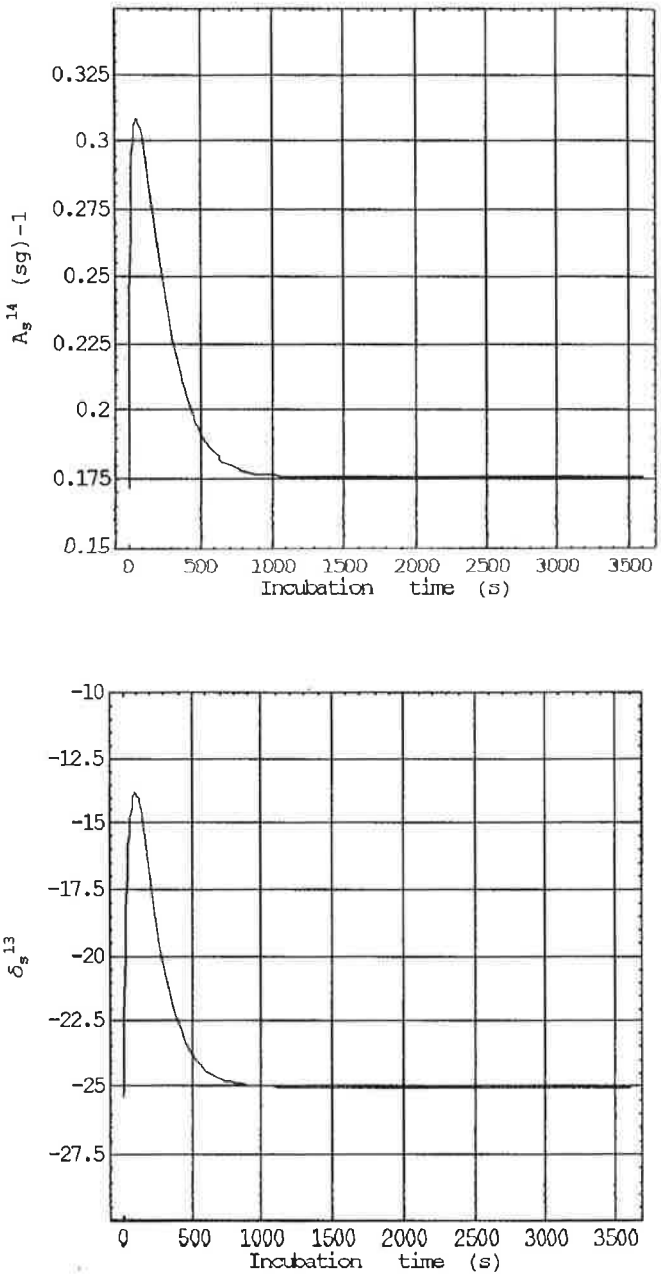


Figure 8.
Computer Simulation of Arizona Esperiment
A_s^{14} (t) (Left), δ^{13} (t) - (Right)
Arizona reported isotopic values at 15.5 hrs (SS,800 s)

Because of the 200 fold increase in the carbon dioxide pressure (and hence concentration), the C-13 and 14 enrichments reached their maximum value in about 100 seconds followed by a return to equilibrium in about 500 seconds [38]. Since the total duration of the Arizona heating experiment was 15.5 hours (55,800 s), it is evident, within the framework of our model that their null result was due to complete equilibration of their En-Gedi sample by the exchange process [39]. As such, we regard the Arizona result as a being consistent with the Russian

data, through the interpretation of our model, rather than the being counterpoised to that data as argued by the authors.

Kouznetsov et al. also present data showing how δs^{13} and As^{14} vary with temperature at a fixed time of one hour. It is of interest to determine if our model can account for this behavior. Taking the analytic solution of Equations (24-27), we assumed that the rate constants vary with temperature according to the usual Arrhenius form,

$$K^m = A_K \, e^{-\frac{E_m}{kT}} \qquad (32)$$

$$K^n = \alpha_E A_K \, e^{-\frac{E_m}{kT}}$$

where

A_K = Associated Arrhenius constant for carboxylation (s^{-1}) [40]

E_m, E = activation energies for carboxylation, exchange

α_E = Ratio of Arrhenius constant for exchange to carboxylation

By fixing the time **t** at one hour and using Equations [32], we may consider Equations (24-27) to be functions of temperature, **T**, for a given activation energy, E_m, Associated Arrhenius constant A_K, and exchange factor α_E. We then varied these three temperature parameters in such a way as to find the best fit of our temperature functions with the given data while fixing the rate constant values to those already deduced at 200 C Figures (9,10) show the best results for δs^{13} **(T)** and As^{14} **(T)** for the following Arrhenius parameters: E_{I2} **= 0.35 eV,** E_{I3} **= 0.33 eV,** E_{I4} **= 0.18 eV, 0.0 eV <E <0.lleV,** A_K **= 2.0 x** 10^{-20} s^{-1}**, 0.0001<** α_E **< 0.001** [41, 42]

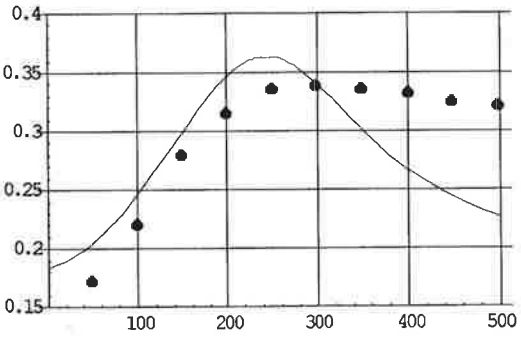


Figure 9. As^{14} $(sg)^{-1}$ **versus temperature (C) Comparison of analytic solution with Russian 1996 data at 1 hr incubation**

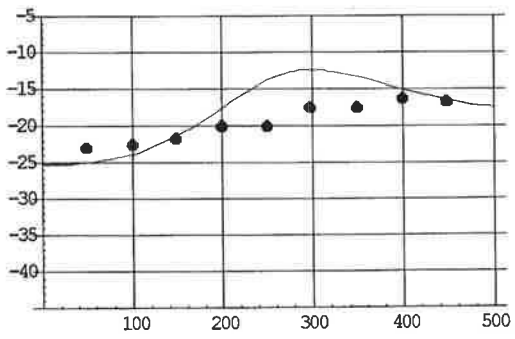


Figure 10. δs^{13} versus temperature (C) Comparison of analytic solution with Russian 1996 data at 1 hr incubation

We first note that the general increasing and then decreasing shape of our temperature solutions resemble those exhibited by the data, particularly for As^{14}. We observe a close match with the rising portion of the As^{14} curve, but the decreasing part is much too steep. The δs^{13} curve is close to the data but with a slight hump in the middle.

We note that our temperature solutions were derived from the analytic model which, as noted above, does not accurately account for the variable amount of C-14 in the chamber. It is not clear how this effect might couple with the more rapid carboxylation rates for C-14 at the higher temperatures. It is also possible that we have overestimated the magnitude of the exchange effect in the temperature range above about 250 C. Let us further recall that in our analytic solution of Equations (24-27), we have explicitly excluded isotope effects in the rate constants for the exchange process and this might conceivably account for the deviation at high temperatures. Nevertheless, with these caveats, we think the agreement of our model with the Russian data is reasonably satisfactory.

It is of interest to compare a standard theoretical model for the Arrhenius constant with the values we have calculated above. For molecular gas collisions, such as we have idealized in this model, the standard Arrhenius term is given by (Ref 10) [43]

$$A = p\sigma \left(\frac{8\,kT}{\pi\mu}\right)^{1/2} \qquad (33)$$

where

σ = collision cross section = 6.6×10^{-15} cm^2 for CO_2 (Ref 10)

$p\sigma$ = reaction cross section (**p** = probability of reaction event)

T = gas temperature (473 K)

μ = (reduced) mass of colliding CO_2 molecules (~ 3.7×10^{-23} g)

Recalling that our associated Arrhenius constant, A_K of 2.0×10^{-20} S^{-1}, is normalized to the chamber volume of

5000 cm^3 via Equation (18), we compute the product of our Arrhenius constant and the volume, $\mathbf{A_K V}$, to be 1.0 x 10^{-16} cm^3 /s.[44] Using Equation (33), we calculate for the same temperature, $\mathbf{A} = (4.4 \times 10^{-10})\ \mathbf{p}$ cm^3 /s. This means that the probability, **p**, of a carboxylating event occurring on a given collision at a specific hydroxyl site is about 2 x 10^{-7}, which means that the reaction process leading to the isotopic enrichment requires very special circumstances at the molecular level for it to occur. In like manner, we estimate that **p** for the exchange reaction, which also involves molecular CO_2 interactions, is α_E times smaller than that for attachment, or approximately 2 x 10^{-10} to 2 x 10^{-11}.

It is beyond the scope of this paper to detail the molecular dynamics involved in the isotopic interaction. It is possible that the events leading to the enrichment occur in several steps, in which case the rate constants that we have calculated represent the ratelimiting step. A successful modeling of the isotopic transfer process will have to explain the comparatively large ratio of the C-14 to C-12 rate constants compared with those for C-13 to C-12.[45] We do note that small variations in the activation energy could be significantly magnified because the ratio E/kT is large (~ 8) and is the argument of the exponential that calculates the rate constant. Note, in particular, that a factor of two differences in the activation energy, $\mathbf{E_m}$, for C-14 relative to C-12, as we calculated above, produced a factor of seventy in their respective rate constants.

Implications for the Shroud of Turin

Considering the very small mass to volume ratio in the Russian experiments (~ lmg / 5000 cm^3), we might tacitly conclude that the Shroud could not have been significantly affected by high temperature isotopic enrichment. In particular, the mass of the Shroud is about one million times larger than the samples used by Kouznetsov et al. whereas the size of the box at the time of the Chambrey fire was only about a factor ten larger in volume[46].

However, there are several very important aspects about this fire event that must not be overlooked and could compensate for the small ratio of box volume to sample mass. First, part of the Shroud fabric was completely burned away while the Shroud was still folded in its silver reliquary. This would create copious amounts of carbon dioxide within the box that could then react with other parts of the intact Shroud. From a consideration of the damage under the patches, we estimate that several percent of the Shroud cloth was consumed in the fire. Moreover, it is likely that a wood inner frame structurally supported the silver box. At temperatures where silver melted (according to eye-witness accounts of the fire) this wood frame would undoubtedly. have begun to smolder and introduce excess carbon dioxide of its own inside the box. When considering these effects, which could introduce relatively high concentrations of carbon dioxide in the vicinity of the Shroud, let us recall that the Russian experiments were performed for 0.03% concentrations of carbon dioxide, the typical amount found in standard air.

While folded in the box, the Shroud was first exposed to heat on its outer layers, primarily by thermal radiation and conduction at contact points with the box.[47] Diffusion then transported heat into the bulk of the folded cloth, giving rise to the repetitive scorch discolorations of similar pattern seen on the Shroud. Because this latter effect takes some time to occur, it is evident that different parts of the Shroud must have been at different temperatures at different times. This could significantly reduce the effective amount of Shroud cloth (i.e. mass) that was able to participate at any given time in the isotopic exchange process at elevated temperatures discussed in this paper.

It is also likely that the box was not air tight because water clearly entered onto the Shroud, presumably when the rescuers of the Shroud tried to cool the box from outside.[48] In addition, reports of certain witnesses to the Shroud fire noted that the box was glowing and had melted somewhat. This surely would have made the box less air tight and therefore more accessible to the outside air, which must have contained significant augmentations of carbon dioxide from the burning church. Thus, the Shroud could have effectively been exposed to a very large volume of air containing carbon dioxide from outside its immediate box environment.

When considering the general yellow color of the Shroud, it is clear that it endured a rather significant thermal event. While we might speculate about the conditions of the 1532 fire, it is noteworthy that carboxyl groups were, in fact, detected by Heller and Adler Ref (15) during their chemical studies of the Shroud samples taken in 1978. In their paper they report, « With the exception of positive aldehyde and cellulosic carboxyl tests, all other species tested negatively... Note that the amido black and Coomassie Blue reactions mentioned above occur, as they also represent the binding of such basic dyes to these cellulosic carboxyls in a manner similar to the methylene blue reaction. This further confirms the presence of such cellulosic carboxyl groups. However, if tested side by side the fibrils can be seen to form a progression with pale yellow fibrils (non-image) staining the weakest, the dark fibrils (scorch) staining the strongest, and the yellow fibrils (body image) giving an intermediate reaction ».

These studies confirm that the Shroud cellulose has been carboxylated. The fact that there is a correlation of carboxylation intensity with the scorches of the 1532 fire strongly suggests that a significant amount of the carboxylation was laid down on the Shroud at the time of the fire of 1532. The Russian experiments indicate that carboxyl formation and radiocarbon enrichment occur simultaneously under temperatures like that expected for the fire event (as evidenced by the Shroud's yellow

color[49]). The calculational modeling of this paper connects the isotope enrichment with the carboxylation process reported by Kouznetsov et al. Thus, there are serious reasons for suspecting that the 1988 radiocarbon date of the Shroud is in error because it is known that the Shroud is carboxylated (most likely from the 1532 fire) and it appears that such carboxylation, under appropriate conditions, could be significantly enriched with radiocarbon.[50]

Conclusions and Recommendations

The calculations and theoretical analyses of this paper obviously depend upon the reliability of the Kouznetsov et al. data. Accordingly, we strongly urge that an independent research team confirm these experiments. In this regard, we find that the University of Arizona's experiment (Refs 4,5) does not, as it stands, constitute a refutation of the Russian work because, as we have shown, the isotopic effect could have been sufficiently transient so as to have been completely missed during their experiment.

We do find that the work of Kouznetsov et al., while lacking certain important critical details necessary for proper theoretical evaluation, does appear to have an internal consistency. We are impressed that those data can be modeled by straightforward rate equations that assume reasonable empirical parameters used by the Russian team (e.g. sample mass, chamber volume, etc.)

It is important to recognize that the burden of proof for the radiocarbon date rests ultimately upon those who have offered this result as an accurate indication of the Shroud's calendar age. If the isotopic phenomenon that has been formally reported by the Russian team cannot be rejected[51], and considering the great uncertainties surrounding the fire of 1532, we submit that the radiocarbon method has probably no real value in establishing the true age of the Shroud of Turin. Moreover, when considering the possible penetration of isotopically enriched carboxylation, molecularly and chemically bonded throughout the cloth cellulose, we further submit that subjecting the Shroud to a further radiocarbon test would be ill advised. ■

ACKNOWLEDGEMENTS

We wish to thank the Fourth World Foundation, Mr. and Mrs. Harry Seggerman, Mrs. Ann Jackson, and Mr. Bryan Walsh for their generous support of this work. We also thank Mrs. Rebecca Jackson for her encouragement and administrative help.

Appendix

In this appendix, we show how the numerical solutions of Equations (14 - 19) vary with the parameters upon which they are based. The purpose is to provide additional insight into the significance of our solution fit to the Russian data. Figure A-1 shows, for easy reference, the solutions for A_s^{14} (t) and δ_s^{13} (t), as given in Figures 4 and 5, of the text that match the Russian data.

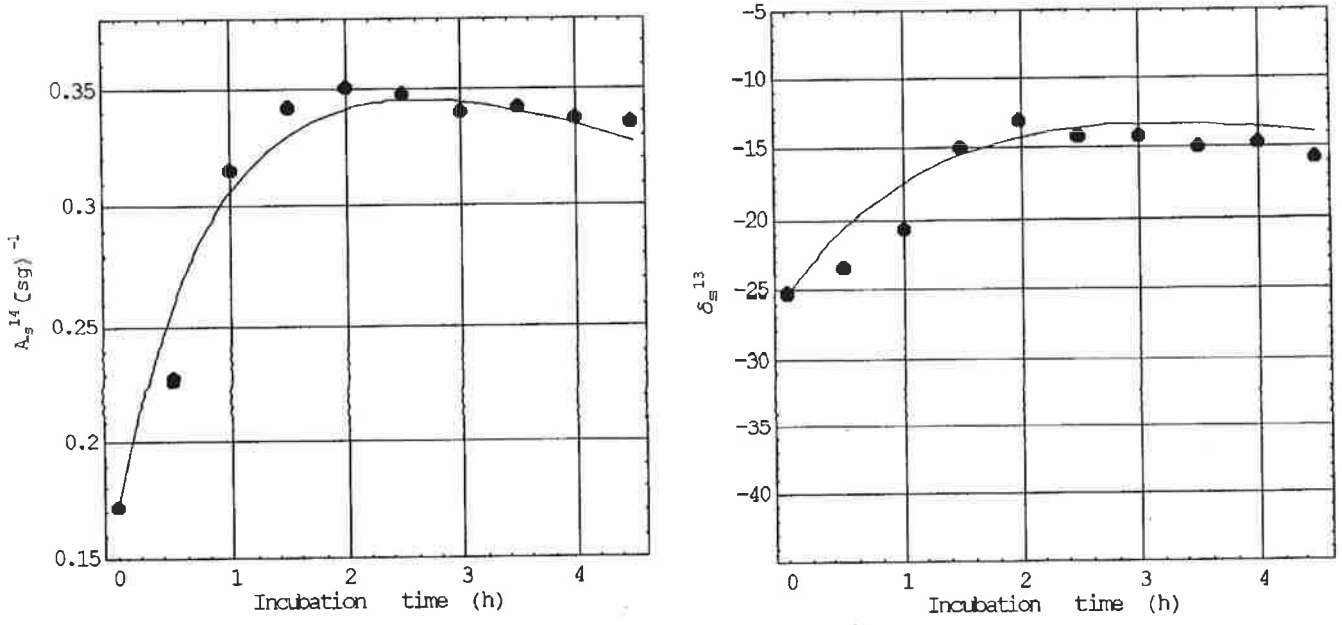


Figure A-1 Numerical solution at 200 C. All parameters identical to that of Figures (4 and 5)

The Figure A-1 solutions are based on the following parameters:

K^{12} = 3.7×10^{-24} s^{-1} (attachment, C-12)
K^{13} = 6.2×10^{-24} s^{-1} (attachment, C-13)
K^{14} = 2.6×10^{-22} s^{-1} (attachment, C-14)
K = 1.4×10^{-24} s^{-1} (exchange)

M = 1.0 mg
V = 5000 cm3
Pc = 20%

$\delta_a 13$ = -12.0
$\delta_a 14$ = -36.5

We now present similar calculations that vary these parameters one at a time from this data set. The resulting solutions can then be compared with the graphs of Figure A- 1.

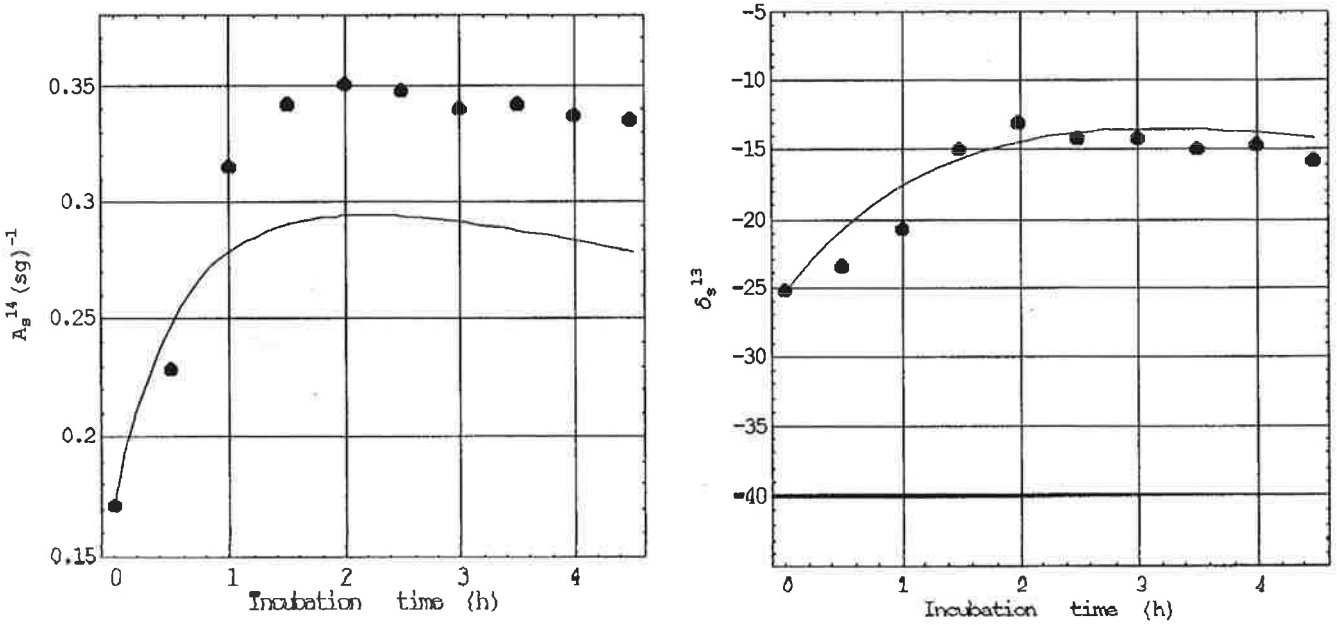


Figure A-2 Numerical solution at 200 C. All parameters identical to that of Figure A-l except M = 2 x 1.0 mg

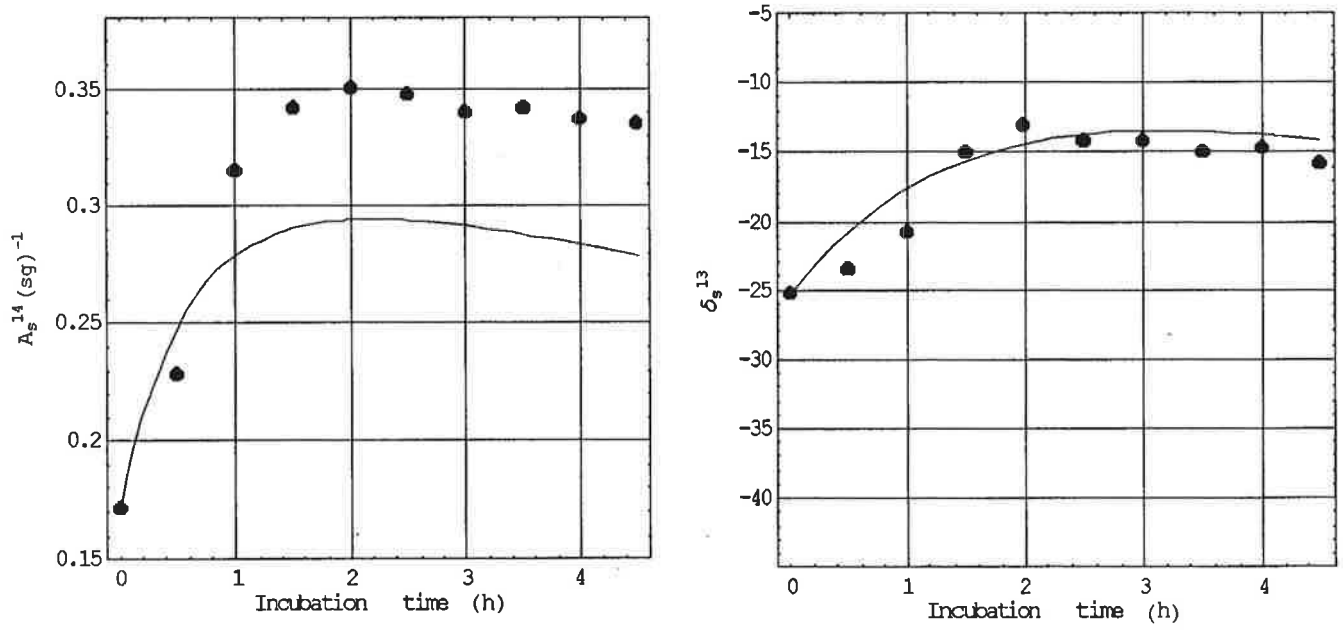


Figure A-3 Numerical solution at 200 C. All parameters identical to that of Figure A-l except.V = 5000/2 cm³

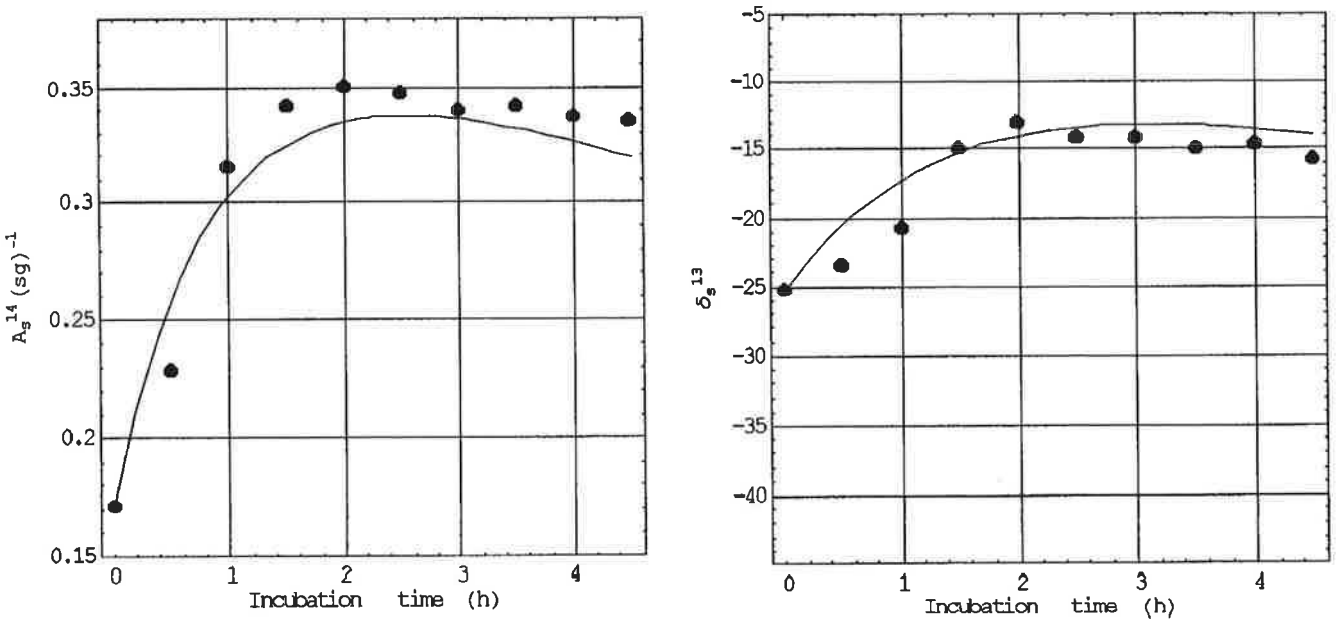


Figure A4
Numerical solution at 200 C.
All parameters identical
to that of Figure A-1 except Pc = 2 x 20%

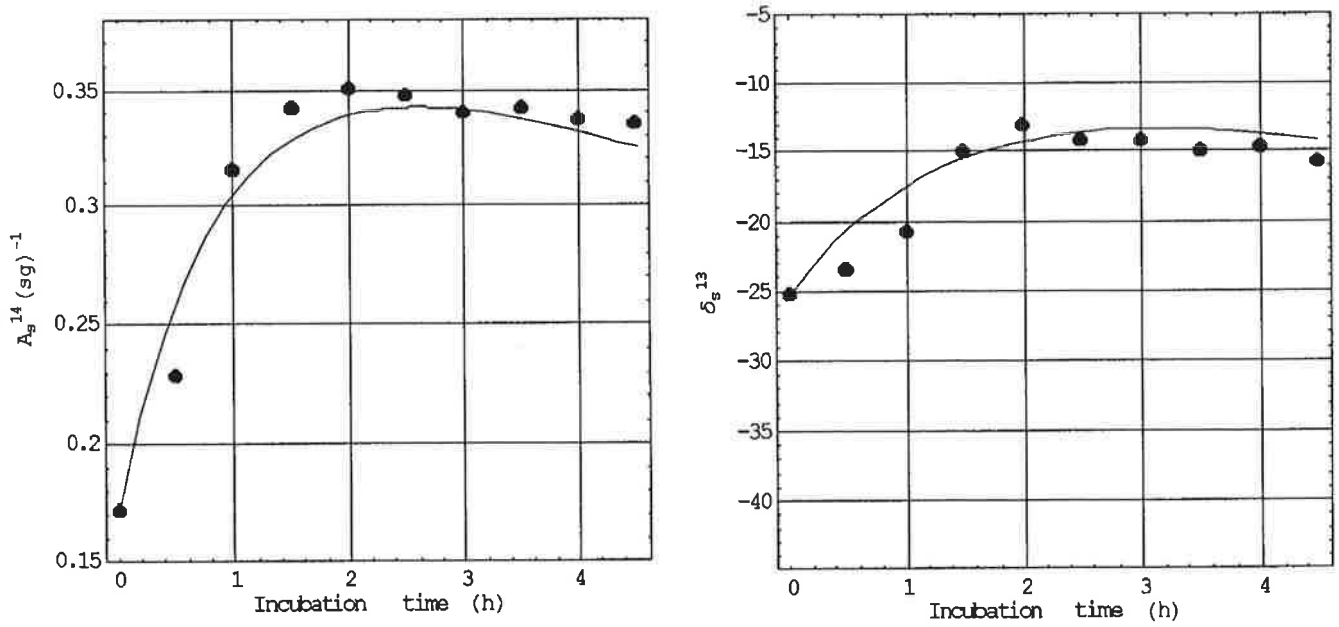


Figure A-5
Numerical solution at 200 C.
All parameters identical
to that of Figure A-1 except
δ_a^{13} = 2 x (-12.0) and d_a^{14}= 2 x (-36.5)

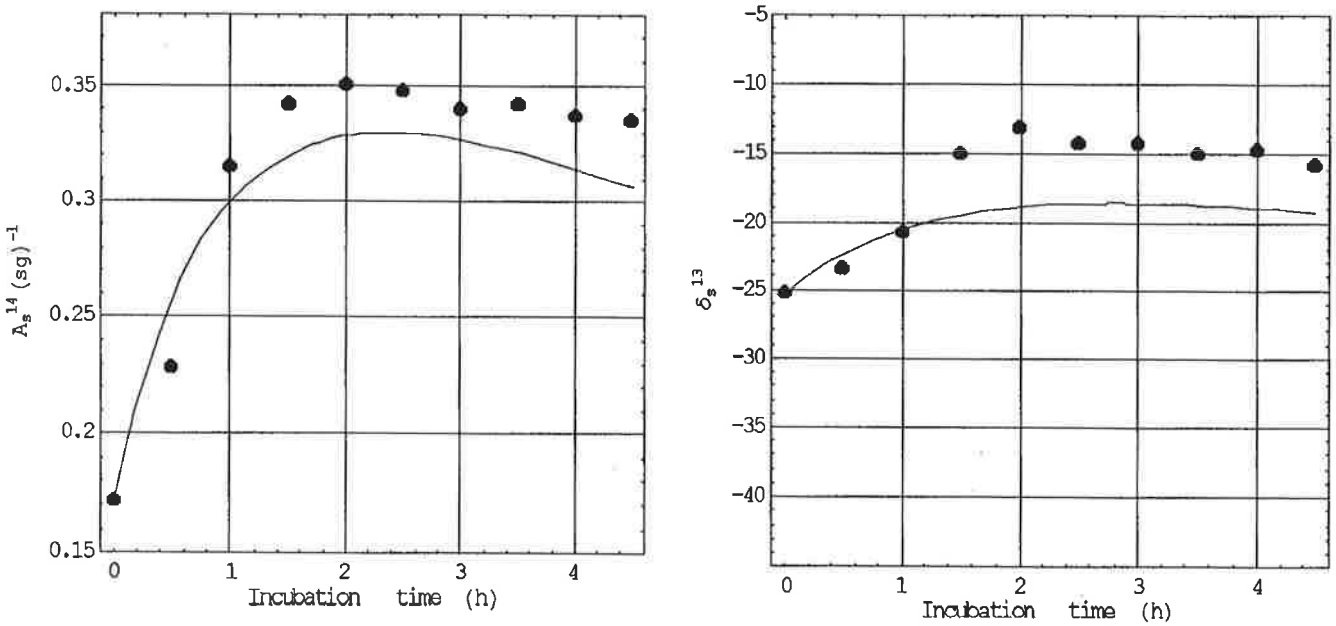


Figure A-6
Numerical solution at 200 C.
All parameters identical to that of Figure A.1 except
$K^{12} = 1.25 \times (3.7 \times 10^{-24}\ s^{-1})$

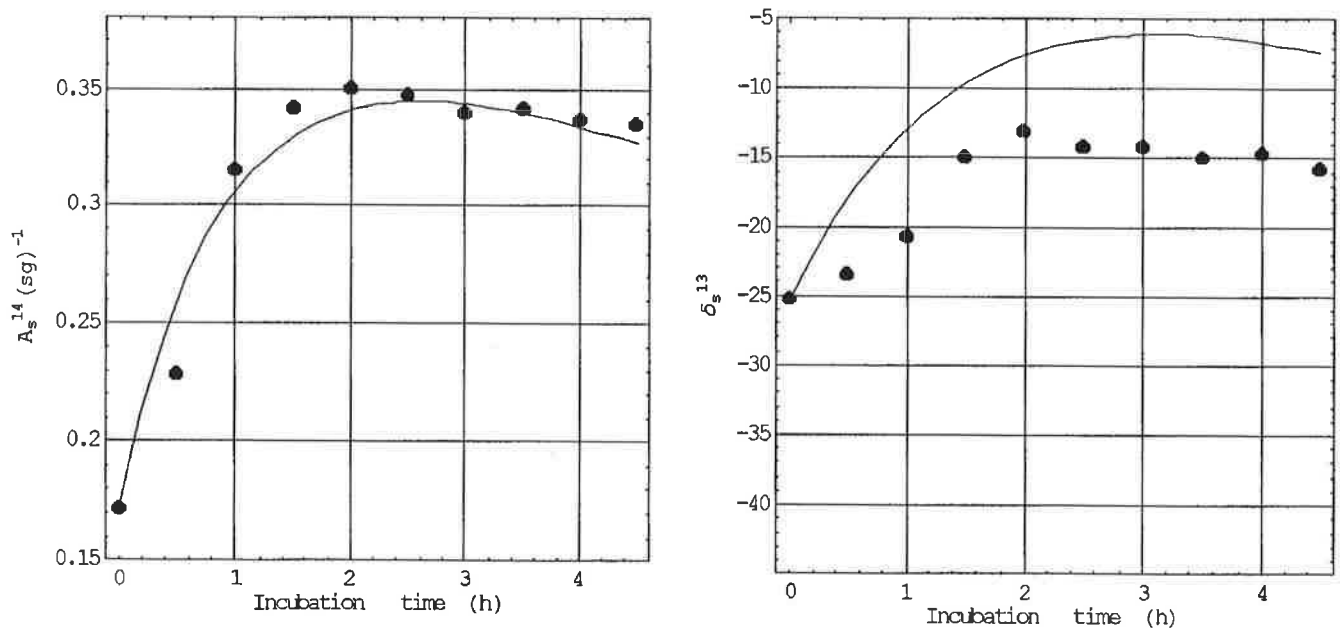


Figure A-7
Numerical solution at 200 C.
All parameters identical to that of Figure A-1 except
$K^{13} = 1.25 \times (6.2 \times 10^{-24}\ s^{-1})$

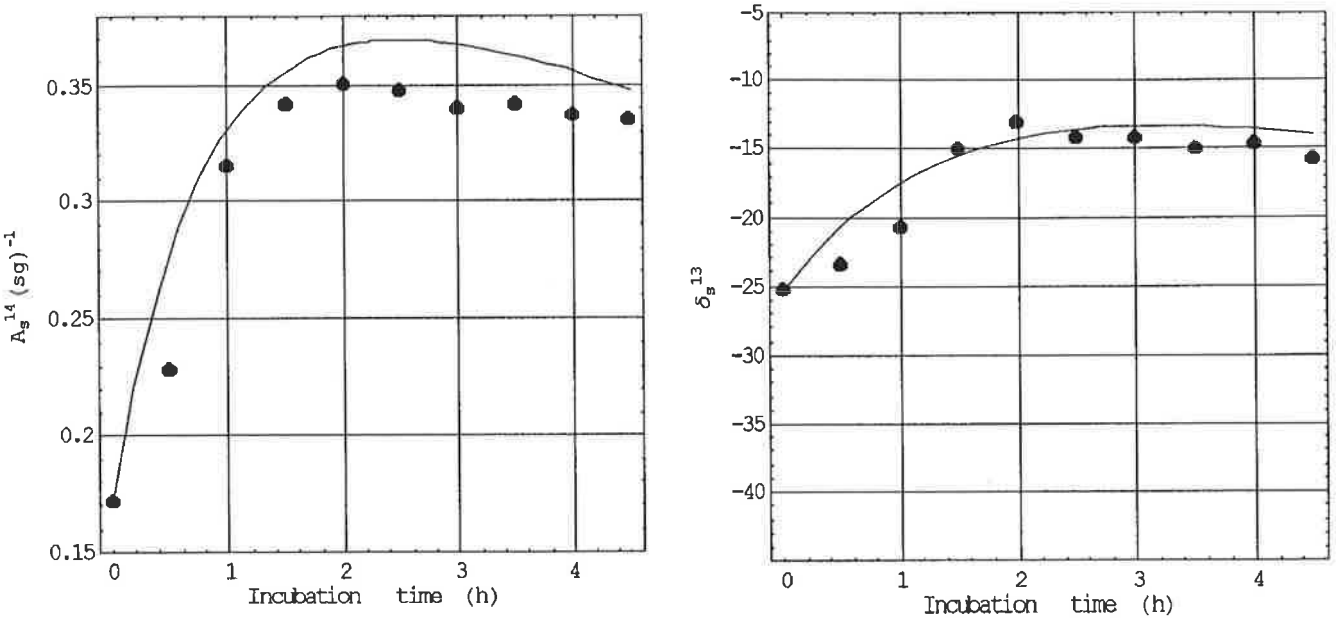


Figure A-8
Numerical solution at 200 C.
All parameters identical to that of Figure A-1 except
K^{14} -1.25 x (2.6 x 10^{-22} s^{-1})

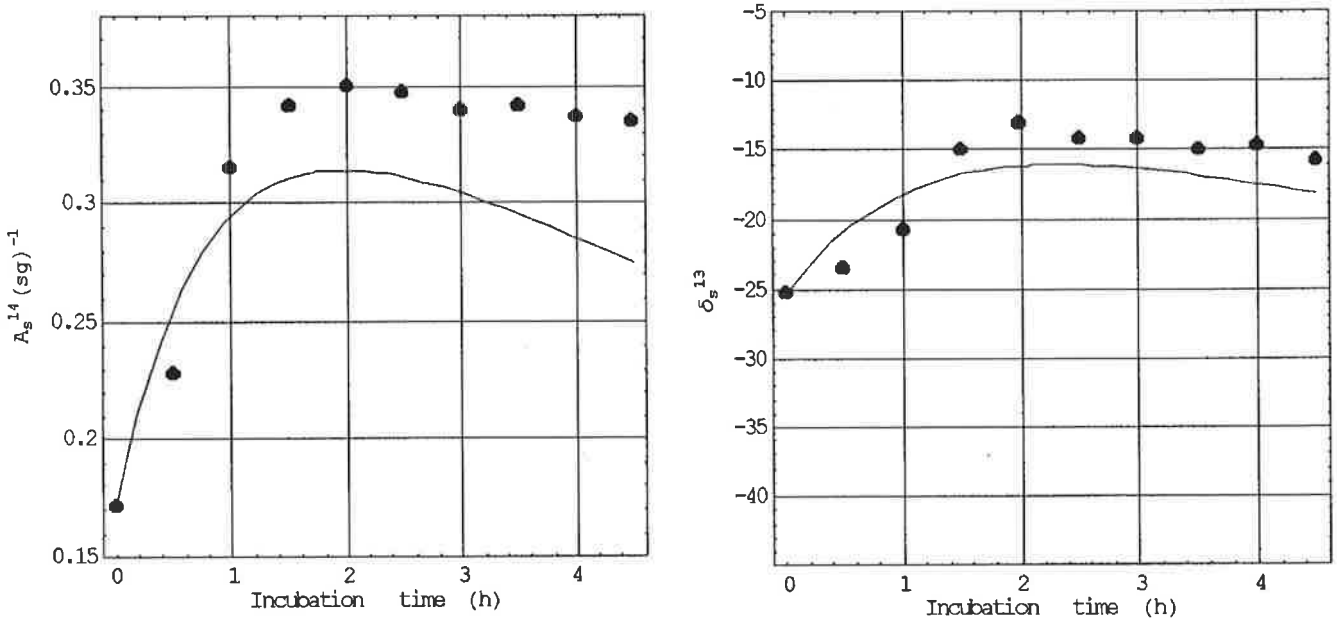


Figure A-9
Numerical solution at 200 C.
All parameters identical to that of Figure A-1 except
K = 2.0 x (1.4 x 10^{-24} s^{-1})

Discussion

In Figures A-2 and A-3 we see that a factor of two increase in the mass of the sample and a factor of two decrease in the volume of the chamber produce the same result, showing that the solution depends upon the ratio (M/V). We also note that the solution for A_s^{14} (t) is sensitive to what is chosen for both M and V, although there is no discernable change in δ_s^{13} (t). This dependence makes sense because it represents a simple scaling of number of sample carbon (M) to air carbon (V).

In Figure A-4 we note that a factor of two increase in P_C produces a small perturbation in the solution for A_s^{14} (t), but not significantly in δ_s^{13} (t).

In Figures A-5 we observe no change in both A_s^{14} (t) and δ_s^{13} (t) when the air deviations, δ_s^{13} and d_a^{14}, are doubled. Thus, the solution is very weakly dependent upon the air deviations, which can also be inferred from Equation (28) for the analytic model.

Figures A 6 through A 8 show numerical solutions for rate constants, K^m (m = 12, 13 l4) that have been increased by 25%. We see that increasing K^{12} decreases significantly both A_s^{14} lt) and δ_s^{13} (t), while increasing K^{13} renders no noticeable change in A_s^{14} (t) but a significant increase in δ_s^{13} (t). An increase in K^{14} increases A_s^{14} (t), while δ_s^{13} (t) is unchanged. These behaviors are easily understood by recalling that A_s^{14} (t) varies approximately as n^{14}/n^{12}, while δ_s^{13} (t) as n^{13}/n^{12}.

In Figure A-9, the exchange rate constant, K, has been increased by a factor of two. We see that the peak values of both A_s^{14} (t) and δ_s^{13} (t) are decreased and the magnitude of the negative late-time slopes have increased. These effects are due to a competition of the exchange and attachment process that determine the maximum rise of A_s^{14} (t) and δ_s^{13} (t). At late-time, the exchange process brings the C-13 and C-14 enrichments relative to C-12 back to equilibrium more rapidly.

Thus, we see that increasing various parameters produce different effects upon the graphical characteristics of A_s^{14} (t) and δ_s^{13} (t). In some cases, one and not the other variable is changed, while in other cases both change together. Still in other cases, the slope of certain parts of the curves is altered. We also see that A_s^{14} (t) and δ_s^{13} (t) are sensitive to small variations of some of the above parameters.

Thus, in view of this sensitivity as well as the diversity of effects associated with these parameters, we think it is significant that using the experimental parameters of M, V, and P_C, associated with the Russian incubation experiment, give a satisfactory solution fit to the Russian data. ■

Notes

(1) We have added the data point at time zero that we calculated from the measured radiocarbon age and carbon-13 to carbon-12 content of the En-Gedi sample (Refs 2,3). Note that the Russian data extrapolates naturally to this initial value. The absence of this datum from the Russian data apparently caused some confusion in the Arizona critique. It appears as though the Russian data point at 0.5 hrs (~ 0.23 dps g^{-1}) was mistakenly interpreted by the Arizona authors to be the initial activity of the ancient En-Gedi sample prior to heating (Refs 4,5). This, of course, would have given the two millennium old En-Gedi sample a near modern date (the activity of modern carbon is 0.225 dps g^{-1} (Refs 4,5))

(2) Also, sample mass, chamber volume and other relevant experimental parameters are not provided in Ref 7 in order to permit a proper comparison with the Figures 1 & 2 data.

(3) e.g. greater C-14/C-12 and C-13/C-12 ratios in air than in linen coupled with significantly higher rate constants favoring exchange of the heavier isotopes.

(4) Chamber volume is not provided explicitly in the Russian papers (Refs 2,3). As discussed below, we obtained the volume via private communication.

(5) This exchange process is assumed to operate only between the air carbon-dioxide and the added carboxyl groups, not on the base cellulose of the sample.

(6) One of us (Jackson) also rnade this assumption to initially argue that carboxylation could not account for the reported isotopic enrichment in linen (San Marino Shroud Conference, Feb 1996). Subsequent consideration of the effect of different rate constants for the three isotopes of carbon led to the studies discussed in the present paper that reverses this conclusion.

(7) The essence of this logic can be seen by considering the following approximate equation, $\mathbf{t = t_s + \lambda\,(t_s - t_c)}$, that relates the actual calendar age, **t** (BP), of a contaminated sample to the overall radiocarbon age, $\mathbf{t_s}$ (BP), of the sample and the effective radiocarbon age, $\mathbf{t_c}$ (BP), of the contarnination taken by itself. λ is the ratio of the number of carbon atoms in the contamination to that in the uncontaminated part of the sample. The Russian team reports (Refs 2,3) incubating the En-Gedi sample of radiocarbon age 2175 BP for one hour at 200 C to change the radiocarbon age to 800 BP, a net change of 1375 years. Thus, if we take $\mathbf{t_s}$ = 800, **t** = 2175, and $\mathbf{t_c}$ = 0 (incubation in modern air), we calculate λ = 1.72. The Russian team reported that 20% of all cellulose monomers are carboxylated once, on the average. Since there are six carbon atoms in cellulose and one in a carboxyl group, a 20% carboxylation corresponds to λ = 0.033 (i.e. 0.2 / 6), a factor of over 50 smaller than that required to explain theradiocarbon shift by carboxylation. However, this argument assumes that the radiocarbon age of the contamination is the same as the air from which it came, which implicitly assumes that the rate constants for attachment are the same for C-12, 13, and 14. If the attachment rate constants for the carboxylation are isotopically dependent, then the effective «radiocarbon age», $\mathbf{t_c}$, of the contamination might be quite different than the radiocarbon age of the air (which we took above to be zero, i.e. modern).

(8) In this paper we use the following values based on standard isotopic abundances: $\mathbf{(n^{13}/n^{12})_{ref}}$ = 0.0112 and $\mathbf{(n^{14}/n^{12})_{ref}}$ =

1.185×10^{-12}. The results of our calculations are not sensitive to what is chosen for these values.

(9) In this paper all numerical values for δ^{13} and δ^{14} will be expressed in part per mil units, as indicated by these equations.

(10) (δs^{13}, $\mathbf{d}s^{14}$), ($\delta_i{}^{13}$, $\mathbf{d}_i{}^{14}$) and (δ^{13}, $\mathbf{d}^{14}$) separate1y satisfy the definitions of Equations (2 ~ 3) if their respective isotopic quantities associated with Equation (1) are inserted.

(11) For a temperature of 200 C (typical of Kouznetsov's experiments), atmospheric pressure, and collision cross-section for carbon dioxide (6.6×10^{-15} cm^2 (Ref 9)), the mean free path is 0.07 microns, about 5/1000 the diameter of a fibril. Crystalline regions within a fibril are typically on the order of 0.01 microns (Ref 9) and it seems reasonable to assume that the microscopic voids into which air molecules diffuse are probably significantly greater than this dimension and therefore on the order of or larger than the mean free path. This suggests that we could use standard gas law physics within the fibril voids.

(12) Pierce (Ref 11) has calculated that at 100% humidity molecular water attaches directly, on the average, to about 80% of the glucose residues in cotton. Crystalline regions account for about 2/3 of cotton material, implying that about 1/3 is accessible to direct absorption by gaseous water vapor on the three hydroxyl groups per glucose residue. Equivalently, this computes to about one hydroxyl group per residue on the average, close to what Pierce calculates. At elevated temperatures (200 C), such attached water is removed from the sample, exposing as many hydroxyl groups for possible carboxyl attachment by atmospheric carbon dioxide. Thus, Kouznetsov's 20% estimate of sample carboxylation is not unreasonable for the amount of hydroxyl sites that might be available according to the above water vapor studies.

(13) As our model does not specify the molecular process by which isotopic attachment occurs, we understand that the rate constant $\mathbf{k}^m$ embodies the net effect of whatever processes are involved. For example, if a series of reactions underly the carboxylation process, then $\mathbf{k}^m$ would represent the rate limiting rate constant.

(14) The above footnote applies also to the exchange process.

(15) This can be seen by adding Equations (9) through (11) to form the relation,

$$\frac{\mathbf{dn}_{total}}{\mathbf{dt}} = (\mathbf{k}^{12}\,\mathbf{n}_a{}^{12} + \mathbf{k}^{13}\,\mathbf{n}_a{}^{13} + \mathbf{k}^{14}\,\mathbf{n}_a{}^{14})\,(\mathbf{n} - \mathbf{n}_{total})$$

where $\mathbf{n}_{total} = \mathbf{n}^{12} + \mathbf{n}^{13} + \mathbf{n}^{14}$. We note that all the exchange terms cancel out, leaving only the attachment terms to change the total number of carboxyls in the contamination. Indeed, when saturation is reached, i.e; $\mathbf{n}_{total} = \mathbf{n}$,

we have $= \dfrac{\mathbf{dn}_{total}}{\mathbf{dt}} = \mathbf{0}$

even though Equations (9-11) still separately allow the relative isotopic concentrations to change via the exchange terms. In otherwords, saturation of the cellulose by carboxyls does not preclude isotopic rearrangements as long as the net carboxylation remains constant.

(16) $\sigma = 6.6 \times 10^{-15}$ cm^2 and $\mu = 3.7 \times 10^{-23}$ g. Note that the total gas pressure is used because CO_2 molecules also collide with other gas species (e.g. nitrogen, oxygen, etc.).

(17) Convection is considerably more effective in mixing gases than diffusion and this wlll significantly reduce the time for smoothing out the carbon dioxide conœntration from what is calculated here for diffusion. Thus, our estimate should be considered an upper time limit for homogeneity in the concentration to occur.

(18) Note that in these equations we have multiplied Equations (9-12) by the volume of the sample to form equations for absolute numbers of carboxyl groups in the sample.

(19) Owing to the age of the En-Gedi sample used in the Russian experiments, it is possible that there existed some prior carboxylation, for example due to microbiological activity (Ref 12). In our model, we exclude this exhaneous carboxylation in our definition for N which strictly represents the total number of sites available for carboxylation from the air at the begirming of the incubation.

(20) This does not mean that the exchange process does not occur, but that the exchange rates are assumed to depend only on the relative amounts of the various isotopes in the air and in the sample.

(21) The air differential Equations (17) are not needed since the carbon-dioxide concentrations are now assumed to be constant in time by virtue of the second condition of Equation Set (20).

(22) The defining calculations below are based on the repetitive structural formula $C_6H_{10}O_5$ of dry cellulose of which 44% of the molecu1e's mass is carbon and contains six carbon atoms per molecule.

(23) We deduced the value for $\mathbf{d}_i{}^{14}$ from the measured radiocarbon age, **t**, of the En-Gedi sample (2175 BP) and the given value for $\delta_i{}^{13}$ (-25.3), using the relations $\mathbf{t = 8033\ In\ [1/(1 + D^{14}/1000)]}$, where $\mathbf{D}^{14} = \mathbf{d}^{14} - \lambda\,(\mathbf{1 + d^{14}/1000})$ and λ, = 2 (δ^{13} + **25**).

(24) One of us (Jackson) visited Kouznetsov's Moscow laboratory in February 1995.

(25) In normal scientific collaboration resorting to this type of methodology is unnecessary, but was due to our complete inability to contact Kouznetsov for the past year. This is unfortunate because sample mass is a critical parameter.

(26) This mass is near the practical limit for AMS dating.

(27) All parameters for that solution will then have been specified by separate and independent pieces of empirically based information that we have shown are necessary to produce a well-defined solution to our rate equations.

(28) We regard this procedure as approximate because the four equations are derived from our analytic solution that assumes the isotopic levels in the chamber do not change significantly (See Equation Set 20 middle). As seen below in Figure 7, this assumption turns out not to be exactly true for C-14 in air. For this reason, we used this procedure only to bring us close to the actual values of the rate constants. The values for the rate constants given here are those that were used in the full numerical integration of Equations (14-17), the solutions of which are shown in Figures 4 and 5 and are based on the empirical parameters discussed above.

(29) MATHEMATICA™

(30) The four characteristics associated with each graph are (1) initial amplitude at time zero, (2) maximum amplitude, (3) tirne of maximum amplitude, and (4) late time slope. To deter-

mine the four constants K^m and **K**, we used the four characteristics, # 2, 3, and 4 for A_s^{14} **(t)** and # 2 for δ_s^{13} **(t)**. This leaves four characteristics, # 1 for A_s^{14} **(t)** and # 1, 3, and 4 for δ_s^{13} **(t)** that we could consider as being associated with other information needed to determine n_{a0}^m and **N**.

(31) We do not need to know the precise experimental values for δ_a^{13} and d_a^{14} in order to perform a meaningfill numerical integration of Equations (14 -17). As can be seen from Equations (28) and (29), n_{a0}^m have a weak dependence on these variables, which do not vary significantly in nature to make a difference in our calculations. Likewise, we do not need to know precisely the values for P_{C02} and T_0, given that the incubation experiment was performed at roughly standard atmospheric conditions. δ_I^{13} and d_I^{14} are not true variables because they are always defined by the time zero values of δ_a^{13} **(t)** and A_s^{14} **(t)** as indicated by the data. Thus, in an a-priori sense, this leaves only **V**, P_C, and **M** as experimental parameters that we absolutely need to know in order to perform a meaningfill numerical integration of our rate equations. We have shown by varying these parameters in full numerical integrations of Equations (14-17), for fixed K^m and **K**, that δ_s^{13}**(t)** and A_s^{14}**(t)** vary according to the ratio **(M/V)** and P_C, while exhibiting very weak dependence on δ_a^{13} and d_a^{14}.

(32) Note from Equations (32) and (33) below that the rate constants depend only upon temperature (apart from a simple scaling on volume as indicated in Equation (18)).

(33) The Russian Experiment (Refs (2,3)) used silver cations to model conditions of the 1532 fire, which occurred in a silver box. This catalyst, however, was not used in the Arizona Experiment. Although the effect of this catalyst is unclear, we do not think it could have had a significant effect on the carboxylation process for the following reason. In the Russian Experiment, the En-Gedi sample was placed in a test tube with water containing a concentration of about lng/cm^3 silver cations (Ref 2). This test tube was then placed in the 5000 cm^3 chamber (Ref 13). At 200 C this water completely vaporized (Refs, 2,3), leaving a silver residue throughout the sample of approximately this concentration. We estimate that for a lmg sample this corresponds to about 1 x 10^{10} silver atoms. The total amount of carboxyl sites according to our calculational modeling of the Russian experiment is, however, 6 x 10^{17}. If we assume, owing to the complete dehydration of the sample due to reported water vaporization at 200 C (Ref 2), that the silver atoms are immobile, then there does not appear to be sufficient silver atoms available by nearly eight orders of magnitude to catalyze the carboxyl reactions at the large number of attachment sites.

(34) The Arizona team reported that a quantity of 1.9 cm^3 CO_2 normalized to 1.0 atmospheres, 25 C was used in their experiment. This normalized volume is equivalent to **n** = 4.6 x 10^{19} CO_2 molecules. Multiplying by 12/ 6 x 10^{23} gives the mass of carbon contained in the CO_2 as 0.92 mg. The Arizona paper (Ref 5), however, gives the mass as 0.93 ng, clearly a mistake in units. This error was also repeated in giving the mass of the sample carbon as 1.44 ng, which actually should be 1.44 mg (3.6mg x 0.4). Arizona indicates that the CO_2 pressure for their experiment was **P** = 0.06 atmospheres and the experimental temperature was **T** = 200C. A simple calculation using ideal gas law gives for the actual experimental volume **V = nkT / P** = 50.0 cm^3. We used this volume to correct the rate constants for C-12, 13, 14, which we deduced from the Russian data at 200 C according to Equation (18), by the relation $K^m_{Arizona} = K^m_{Russian}$ (5000/50).

(35) We calculated the deviations d^{14} for air and linen from the reported values by Arizona (Refs 4,5) for δ^{13} (-17.8 air, - 25.3 linen) and fraction of modern carbon F_m (1.35 air, 0.7609 linen) before incubation, using the formula, $d^{14} = \{ [(F_m - 1)1000 + \lambda] / (1 - \lambda/1000) \}$ where $\lambda = 2 (\delta^{13} + 25)$. This relation comes from the two ways that radiocarbon age may be calculated, $t = -8033 \ln (F_m) = 8033 \ln [1/(1 + D^{14}/1000)]$, where $D^{14} = d^{14} - \lambda (1 + d^{14}/1000)$.

(36) We used the Russian 20% carboxylation factor because the Arizona Laboratory used for their sample the same En-Gedi textile employed by the Russian experiment (for which we successfillly used the 20% value).

(37) The air diffusivity for the conditions of the Arizona experiment (0.06 atmospheres, 200 C), according to Equation (13) is about 2.5 cm^2/s. The diffusion time for a 50 cm^3 volume of cubic linear dimension 3.2 cm is about (1/2)(3.2 cm)^2/ 2.5 cm^2/s = 2 seconds, considerably shorler than the several hundred second time, characteristic of the isotopic changes calculated here for the Arizona experiment. Thus, our assumption of isotopic uniformity that underlies the rate Equations (14-17) is valid for the Arizona simulation.

(38) The Arizona team (Refs 4,5) note that their experiment should proceed 200 times faster than that of the Russian experimenters, due to the relatively high concentrations of CO_2 used in their experiment.

Accordingly, they imply that if isotopic enrichment occurs, it should have occurred 200 times more rapidly in their experiment than in the Russian study. Moreover, they ran their experiment over three times longer than the Russian team. In spite of these augmentations, the Arizona team failed to observe any significent isotopic enrichment. However, a close inspection of the Russian data (Figures 1 and 2), shows that both δ_s^{13} and A_s^{14} decrease slowly after reaching a maximum at about 2 hours incubation. Apart from whatever process underlies the isotopic phenomenon reported in the Russian study, we should expect that the 200 factor speedup should logically apply to the late time «de-enrichment» process as well. We estimate that the late time slope in Figure 1, dA_s^{14}/dt, is about 2.2 x 10^{-6} (s^2 g)$^{-1}$. Thus, the extrapolated time, Δt, for A_s^{14} to return to its initial value, a change of $\Delta A_s^{14} = (0.17 - 0.35) = - 0.18$ (s g)$^{-1}$, is $\Delta t = \Delta A_s^{14} / (dA_s^{14}/dt) =$ 81,800 s or 22.7 hours. A reaction speedup by a factor of 200 gives an extrapolated equilibration time of 400 seconds, considerably shorter than the 15.5 hours of the Arizona incubation. Our numerical simulation of the Arizona experiment, shown in Figure 8, is consistent with this time estimate.

(39) It is of interest to compare quantitatively the values for δ^{13} and F_m predicted by our numerical model at the 15.5 hour (55,800 s) point at which the Arizona team report their measurements (Refs 4,5). At this late time point our computer simulation calculates δ^{13} (-17.8 air, -25.1 linen) and F_m (1.35 air, 0.7801 linen). The starting values (reported by Arizona and used in our calculation) were δ^{13} (-17.8 air, -25.3 linen) and F_m

(1.35 air, 0.7609 linen). The final empirical values reported by the Arizona team (Refs 4,5) were δ^{13} (-17.8 air, -25.9 linen) and F_m (1.30 air, 0.7649 linen). According to our calculations, the initial air values for δ^{13} (-17.8) and F_m (1.35), which changed significantly during the first several hundred seconds of the incubation process, return to their pre-incubation values at the late time of 15.5 hours. We note that the Arizona experiment also displays this late-time to initial equivalence for δ^{13} in air, although F_m does change somewhat. That this happens can be seen from a consideration of Equations (14-17). If we set the time derivatives to zero (corresponding to the steady state condition at late time), we can form a set of algebraic equations that, when used with the conservation equations $N_a^m + N^m = N_{a0}^m$ (**m** =12, 13, 14), show that δ^{13} and F_m for air at late time are equal to their initial air values. The δ^{13} and F_m values for linen do change, however, in our calculation at late time, even though the corresponding quantities in air do not. This is because, as we have just shown for late time, the contarnination takes on the isotopic characteristics of the initial air (due to equilibration by the exchange process). When the associated deviations for the equilibrated contamination are added to those of the base linen, as per Equations (4 and 5), the overall sample deviations change accordingly. The Arizona team, however, attributes the small changes in δ^{13} and F_m in the sample to the expulsion of certain (unspecified) volatiles from the linen sample to the surrounding carbon dioxide environment. The associated changes in δ^{13} and F_m that they report are of such magnitude that they could easily mask some or all of the isotopic effects that our model calculates at late time, which are of the same order.

(40) In standard useage, the Arrhenius constant, **A**, pertains to rate constants appropriate for concentration variations as in Equations (9-11). However, here we define an associated Arrhenius constant, A_K in terms of the rate constant, K_m that we used to track absolute amounts of isotopic quantities in the closed system of volume, **V**, as in Equations (14-16). A simple consideration of Equation (18) shows that $A_K = A/V$.

(41) If α_E is too small, then the computed activation energy becomes negative; too large, then the high temperature fit becomes worse.

(42) The Russian time and temperature data (Figures 6 and 7 - Ref 2) are inconsistent as published. The value of A_s^{14} at 200 C, 1 hr in Figure 6 (Ref 2) is about 0.33, whereas in Figure 7 (Ref 2) for the same temperature and time A_s^{14} is less than 0.32. We attribute this data inconsistency to a simple plotting error in Figure 6 (Ref 2) because a simple right shift by 50 C, the incremental spacing of the data samplings, resolves this discrepancy. We have therefore incorporated this shift into our Figure 9 representation of the Russian data (Compare Figures 1 and 9 at 1.0 hour, 200 C). There is, however, no such inconsistency in the δ_s^{13} data of Figure 8 (Ref 2), our Figure 10.

(43) Strictly speaking, this formula applies to gas phase reactions. Here, we are modeling a gas/solid interaction. Nevertheless, if we crudely consider the hydroxyl molecules at the attachment sites distributed throughout the sample as a «gas» that interacts with the surrounding carbon dioxide gas, we should be able to use this simple formula to make certain estimates concerning the nature of the isotopic reaction.

(44) Recall that $\mathbf{A} = A_K\mathbf{V}$; see footnote 40.

(45) We are considering several ways in which this might occur.

(46) The areal density of the Shroud linen is about 20mg/cm2; dimensions are 434 x 109 cm. The Shroud was folded 48 times at the time of the fire as inferred from the burn patterns on the cloth.

(47) The two long burn lines along the length of the Shroud are most likely due to direct heat contact of the folded Shroud with the sides of the box. The flared scorch discolorations alongside the face are likely due to thermal radiation.

(48) This water was probably not used to extinguish the burning part of the cloth because, in reconstructions of the 1532 fire, the waterstains accumulate on the opposite side from the burn areas as seen from a top view of the folded Shroud

(49) One of us (Jackson) has characterized quantitatively cloth yellowing at temperatures above and below 200 C (Ref 16).

(50) The conditions of the 1532 fire as they relate to possible isotopic enrichment need to be better understood. Important information about the 1532 fire is contained in the discololoration and burn patterns found on the Shroud. There are also eye-witness accounts available.

(51) It is essential that independent laboratory verification of the Russian results be made. It is also important to understand the molecular basis for the reported isotopic phenomenon in order to have a full understanding of the underlying process. Moreover, the range of possible parameters of the 1532 fire should be clarified in order to better evaluate the effects of the reported isotopic enrichment on the Shroud. Finally, it is important to study the carboxylation characteristics of the Shroud itself, if feasible, in order to determine if this contamination is, indeed, enriched with radiocarbon. To these ends, we are open to collaboration and could offer our code modeling to help design appropriate experiments. We also intend to continue with our own studies of the above issues.

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L'influence de l'incendie de 1532 sur la datation du Linceul par le radiocarbone

Il a été suggéré que l'incendie de 1532 était responsable d'un apport suffisamment significatif de radiocarbone provenant de l'air environnant pour expliquer la datation médiévale du Suaire donnée en 1988. Des résultats russes publiés rapportent l'observation d'un tel effet, bien que le laboratoire de l'université d'Arizona ait échoué pour donner la confirmation nécessaire du travail russe. Cet exposé fait le bilan de cette différence, et présente des études scientifiques qui évaluent la consistance interne des données russes. Les résultats de cette analyse sont alors utilisés pour évaluer l'importance de l'hypothèse de l'incendie dans l'explication de la date médiévale donnée par la datation au C 14.